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DEVELOPMENT OF TECHNIQUES FOR DETECTION OF LOW MOLECULAR WEIGHT
CONTAMINANTS IN PRODUCT WATER FROM WATER PURIFICATION
OR WATER RE-USE SYSTEMS

FINAL COMPREHENSIVE REPORT

Thomas W. Mix
Hans Scharen

August 1976

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LOW MOLECULAR WEIGHT CONTAMINANTS IN PRODUCT
WATER FROM WATER PURIFICATION OR WATER RE-USE SYSTEMS

Thomas W. Mix
Hans Scharen

Supported by

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Washington, D. C.   20315

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Amicon Corporation
25 Hartwell Avenue
Lexington, Massachusetts 02173

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Ozone	Instrumentation	
TOC	Wastewater	
Total Organic Carbon	Permanganate	
MUST	Carbon Adsorption	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A permanganate colorimeter instrument to monitor the quality of MUST product water has been developed and successfully tested at the breadboard level. During the program it was demonstrated that (1) aldehydes are the last of the constituents of MUST RO permeate to be ozonated, (2) residual MUST aldehydes (principally acetaldehyde) rapidly reduce permanganate solutions, and (3) the degree of permanganate reduction may be easily quantitated colorimetrically and is directly proportional to residual MUST water contamination. The colorimeter and required hardware is judged low-cost, rugged, simple, and reliable.

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I.   SUMMARY

For three years Amicon Corporation has been under
contract to the U. S. Army Medical Research and
Development Command for the Development of Techniques
for Detection of Low Molecular Weight Contaminants in
Product Water from Water Purification or Water Reuse
Systems.

Principal emphasis during the latter portion of the
program has centered on the development of a permanganate
colorimeter instrument to monitor the quality of MUST
product water which has been processed through both
reverse osmosis and ozonation. The selection of the
permanganate colorimeter was based on a number of
factors:

1. The rate limiting step in the ozonation of the
    MUST RO permeate appears to be the ozonation
    of aldehydes (acetaldehyde, in particular).
    These aldehydes may therefore be expected to
    accumulate and to represent an appreciable
    fraction of the TOC in the product water;

2. Aldehydes are rapidly oxidized by basic
    permanganate solutions (as are alcohols and
    many other organic compounds);

3. Permanganate and manganate ions have high
    extinction coefficients and are rapidly
    detectable in low concentration spectro-
    photometrically; and

4. A colorimeter is compatible with the require-
    ments for low cost, ruggedness, simplicity,
    reliability, and field operation.

In addition, the technique offers the fail-safe backup
of a simple color comparator.

Initial testing of a breadboard colorimeter with a MUST
pilot unit tends to confirm the suitability of the
technique for MUST product quality monitoring but is
insufficient in scope to establish it with the requisite
certainty. Additional work with MUST pilot plant samples
and with known or suspected contaminants is therefore
recommended.

Additional work done under the program deals with the
following subjects:

1. A preliminary investigation of a spectrophoto-
    meter technique to monitor the rate of decay
    of ozone concentration as a measure of product
    water purity.

2. Carbon adsorption experiments related to monitoring of carbon column adsorption when this was a processing step under consideration for the MUST; and

3. A preliminary study of the monitoring of the combination of reverse osmosis and ozonation and/or carbon adsorption as tertiary treatment steps for the output from a municipal treatment plant.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (continued)

II. OZONATION STUDIES

A. Ozonation Equipment

The apparatus used for the ozonation studies is shown in Figure 1 and consists of a four-necked reaction flask containing a high shear stirrer, a gas dispersion tube, a sample withdrawal tube, and a thermometer. An automatically-controlled temperature bath was used to keep the temperature within $\pm 1^{\circ}C$ of the reaction temperature. The ozone was generated by a Welsbach Ozonator (Model T-816) with an ozone production rate of 1.7% by weight or 16 g/hour using oxygen. In order to make the system airtight, all the joints were fitted with Teflon sleeves. A special shaft of stainless steel with a Teflon bearing was machined for the high shear dispersator disc. Stainless steel, glass and Teflon were used as piping material since they are all resistant to attack by ozone.

B. Experimental Procedures

Ethanol Ozonation

A 100 ppm solution of ethanol was added to the reaction flask and ozonated for three hours. Samples for TOC analysis and ethanol determination were withdrawn periodically every 30 minutes; the last sample being taken at 180 minutes. All TOC analysis was performed at Fram Corporation, Pawtucket, Rhode Island. For TOC analysis, a Beckman TOC Analyzer was used. Ethanol concentrations were determined by oxidizing with acidified dichromate and measuring the disappearance of the characteristic dichromate color at 549 nm with a spectrophotometer. The O.D. values obtained were then compared to a previously prepared standard reference curve from which the actual concentration in mg/liter was read[1]. Ozonations of acetic acid, acetaldehyde, quinone, oxalic acid, formaldehyde, methanol, glycine, and MUST RO permeate were performed in a similar manner. A 100 ppm solution of each compound was prepared. They were ozonated for three hours each and samples were withdrawn for TOC analysis. A portion of the acetic acid sample was used for titration with sodium hydroxide and a portion of the quinone sample was used for the spectrophotometric determination of quinone (Figure 2). The ozonation conditions typically used were: the ozone concentration, 38 mg/liter; gas flow, 0.5 liters/minute; and the reaction temperature, $60^{\circ}C$.

-11-

FIGURE 1

OZONATION TEST SET-UP

λ max. 245 nm

● Standard Curve

▶ Quinone samples after treatment with ozone

mg/1
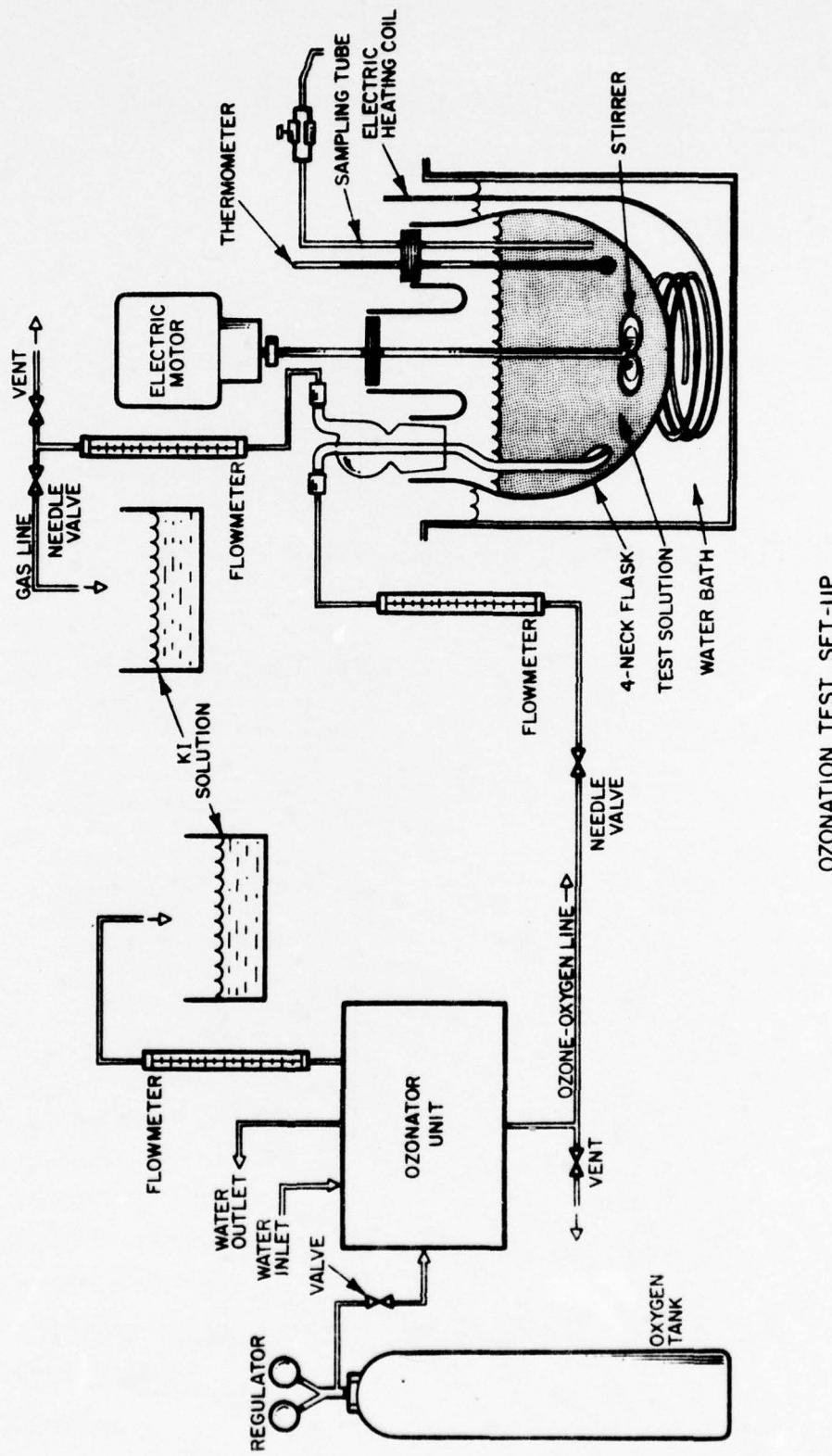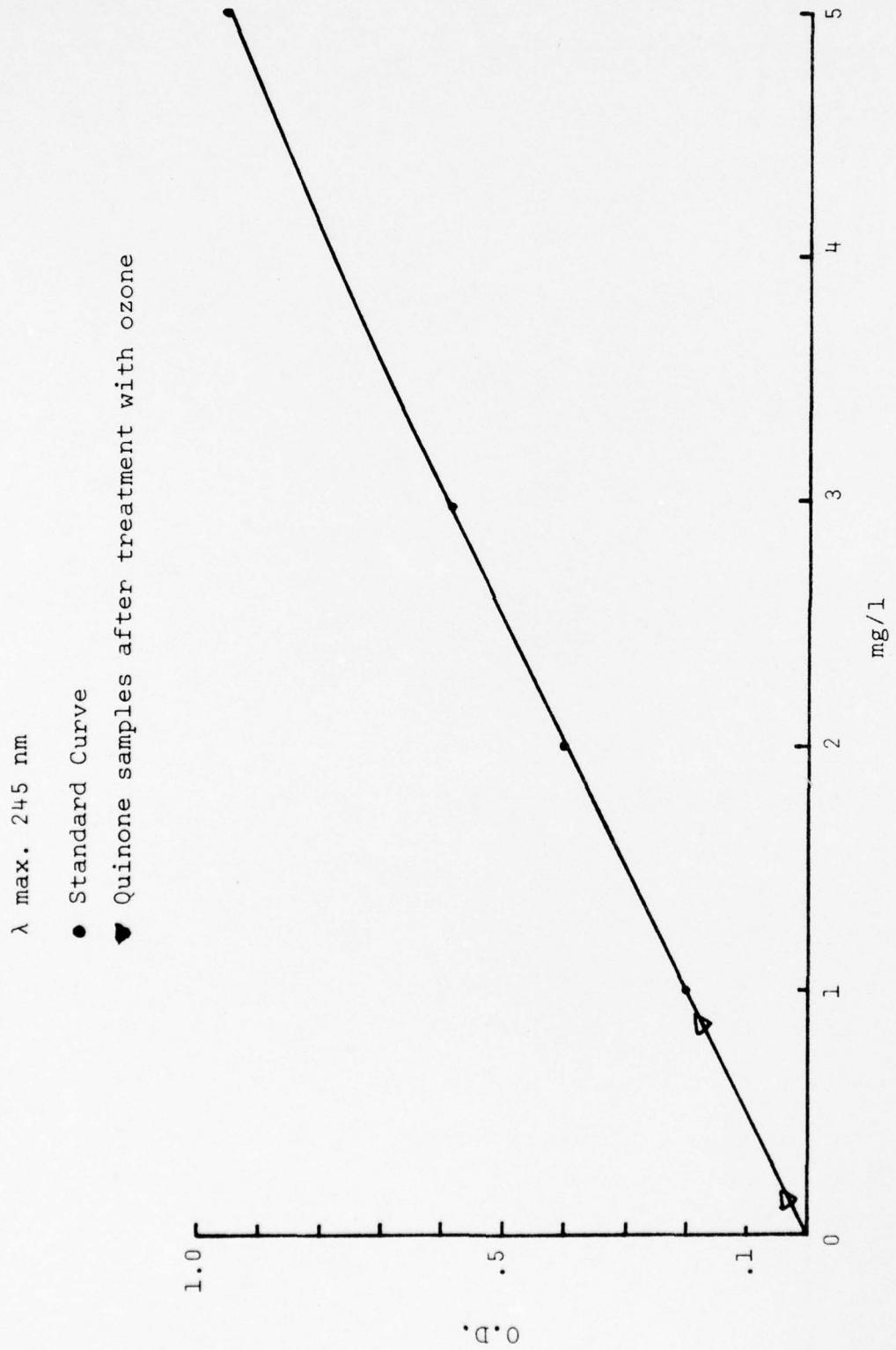
FIGURE 2

DETERMINATION OF QUINONE

O.D.

C. Interpretation of Data

Figure 3 presents curves for the disappearance of
TOC with time for a number of chemicals which were
selected as candidate tracers for a variety of
reasons.

Ethanol and methanol were selected because they have
been identified as principal contaminants in typical
MUST reverse osmosis permeate[2,3]. Acetaldehyde,
acetic acid, and oxalic acid were selected because
they are potential compounds formed in the progressive
oxidation of ethanol and possibly other alcohols.

Formaldehyde was selected because it is likely to be
formed in the ozonation of methanol.

Acetic acid was also selected because Professor
Wiberg of Yale University[4] pointed out that it is
frequently part of the oxidation pathway for ali-
phatic compounds (and aromatic compounds where ring
opening occurs) and is likely to be the most oxidation
resistant step in the pathway. Similarly, quinone was
selected because it is frequently the rate limiting
step in the oxidation of many aromatic compounds[4].

Glycine was selected because amino acids can be detected
in very small concentrations through use of fluorescent
dye indicators, such as Roche's Fluram[5]. The rapid
oxidation of both glycine and quinone makes them un-
suitable as tracers. The normally oxidation-resistant
quinone is probably susceptible to attack by ozone
at its double bonds. Acetic acid is also not useful
as a tracer but for a different reason: it is
essentially impervious to attack by ozone. Since
MUST reverse osmosis permeate is susceptible to
oxidation by ozone and does not show a sufficient
lowering of pH during ozonation to indicate appreciable
accumulation of acid, acetic acid is not formed to
any significant extent during MUST permeate ozonation
at neutral pHs. Because of acetic acid's inertness,
it can be tolerated by the body in fairly high con-
centration, making its removal from the MUST water
to be recycled of limited importance.

Oxalic acid, which is a likely intermediate in many
of the oxidation sequences, is relatively rapidly
ozonated, which is also consistent with the slight
change in pH as ozonation proceeds. Methanol and
formaldehyde also disappear relatively rapidly under
ozonation conditions. The broad scatter in the
formaldehyde data (Figure 4) is not understood but
may perhaps be attributable to some polymeric
material or particulate impurities in the formaldehyde
solution used.

OZONATION STUDIES

FIGURE 3

Figure 3 plots TOC (mg/l) versus Time (minutes) for Acetic Acid, Ethanol, Acetaldehyde, Glycine, Quinone, and Oxalic Acid.
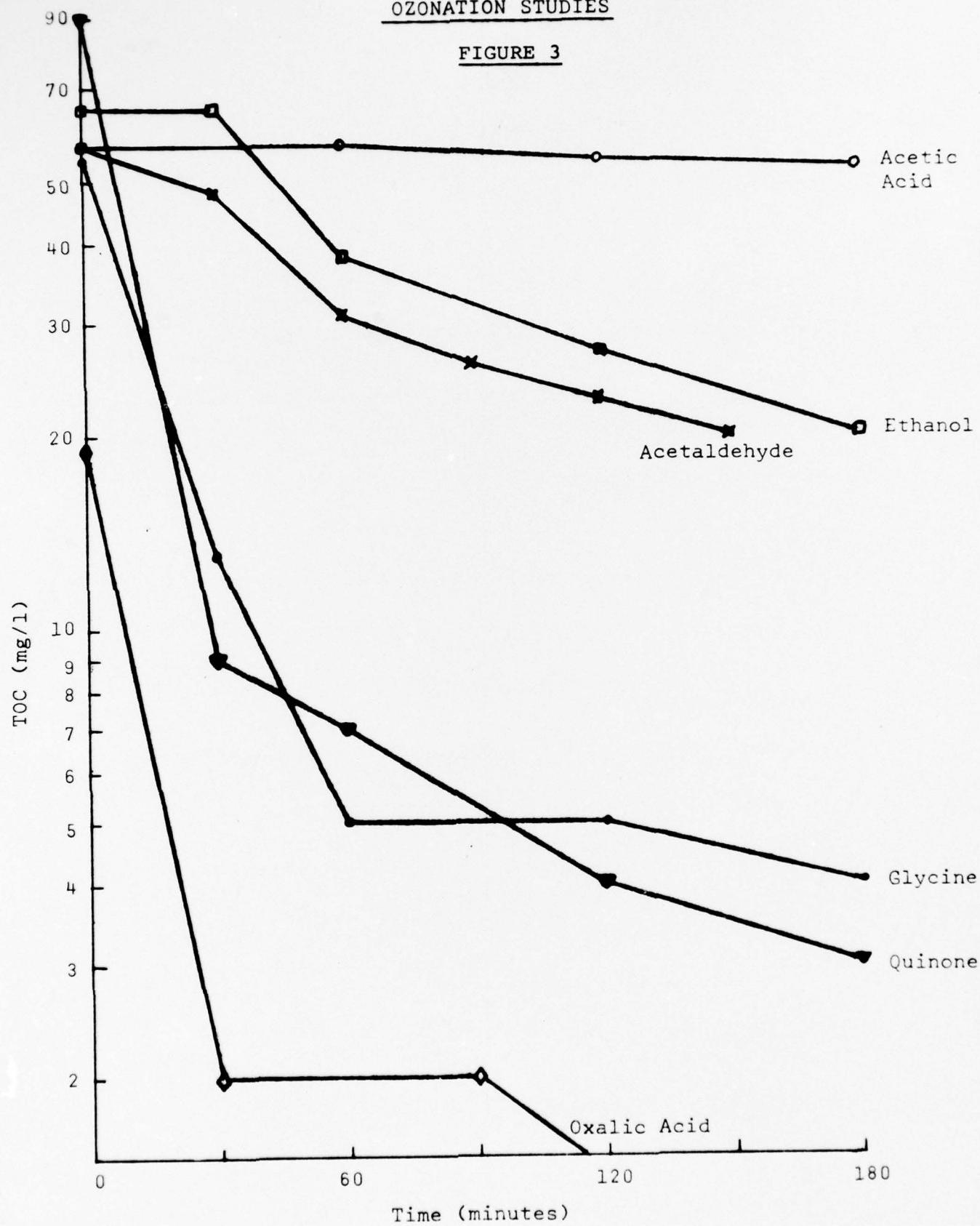
FIGURE 4

OZONATION OF FORMALDEHYDE @ 60°C

Oxygen Rate = 0.5 l/min.
Ozone Concentration in Oxygen = 38 mg/l
Volume Liquid = 1 liter

TIME (minutes)
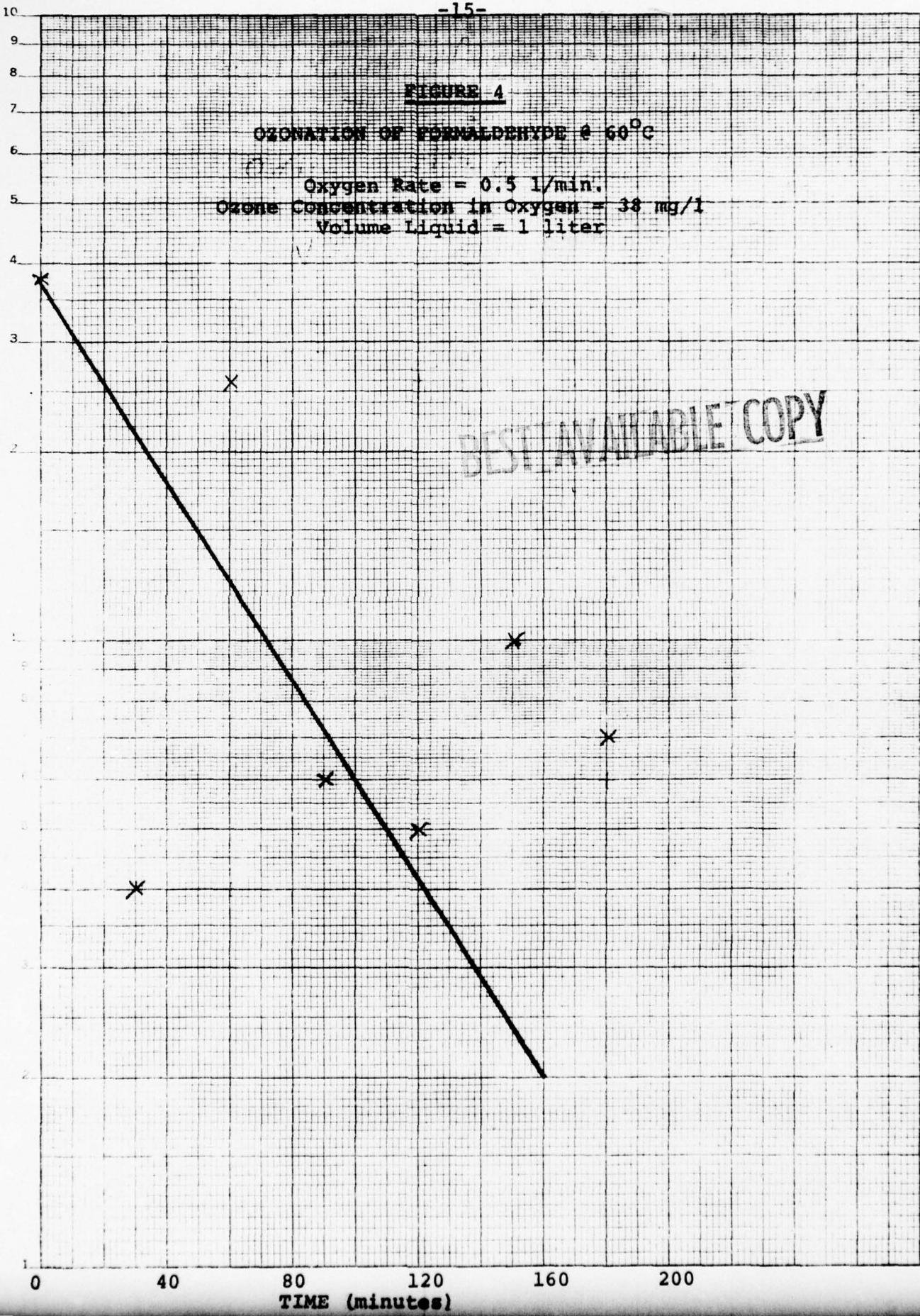
Both ethanol and acetaldehyde, however, have TOC disappearance characteristics quite similar to those of the MUST RO permeate (Figure 5). The similarity among the three TOC disappearance curves suggests that acetaldehyde disappearance is the rate limiting step for all three. This is confirmed by studies of the rate of ethanol disappearance using potassium dichromate which is specific in the time allotted for reaction[6]. The rate of disappearance of ethyl alcohol during ozonation, as measured by dichromate disappearance, shown in Figure 6, is much more rapid than the rate of intermediary oxidation product of ethanol which is relatively resistant to ozonation. There are two possible pathways for ethanol oxidation: one is through acetaldehyde to oxalic acid, which is favored by basic conditions, and the other to acetic acid, which is favored by acidic conditions. The measured pH of the ethanol solution before and after ozonation and the known dissociation constants for acetic and oxalic acids indicate that after ozonation, these acids, if present, should be completely ionized. Their concentration may, therefore, be estimated from the pH since electrical neutrality requires that the anion concentration equal the difference between the hydrogen ion concentration and the hydroxyl ion concentration. This difference is small enough to indicate that there are only negligible levels of either acetic acid or oxalic acid present. Acetaldehyde does, therefore, appear to be the rate limiting step in the ozonation of ethyl alcohol to CO_2 and may, therefore, be an appropriate monitor through which the effectiveness of the ozonation step may be followed provided a sensitive enough method of detection can be developed.

The rate of volatilization (gas stripping) of acetaldehyde may be estimated from its known activity coefficient at infinite dilution[7] and vapor pressure[7] using the equation:

$$\ln (x_i/x_t) = \frac{G \alpha P^0}{V \pi} \tag{1}$$

where x_t = concentration of acetaldehyde in water at time, t

x_i = initial acetaldehyde concentration

G = oxygen supply rate, g moles/min

V = liquid reservoir holdup, g moles

FIGURE 5

Temp.   60°C
O₃ Conc. 38 mg/l
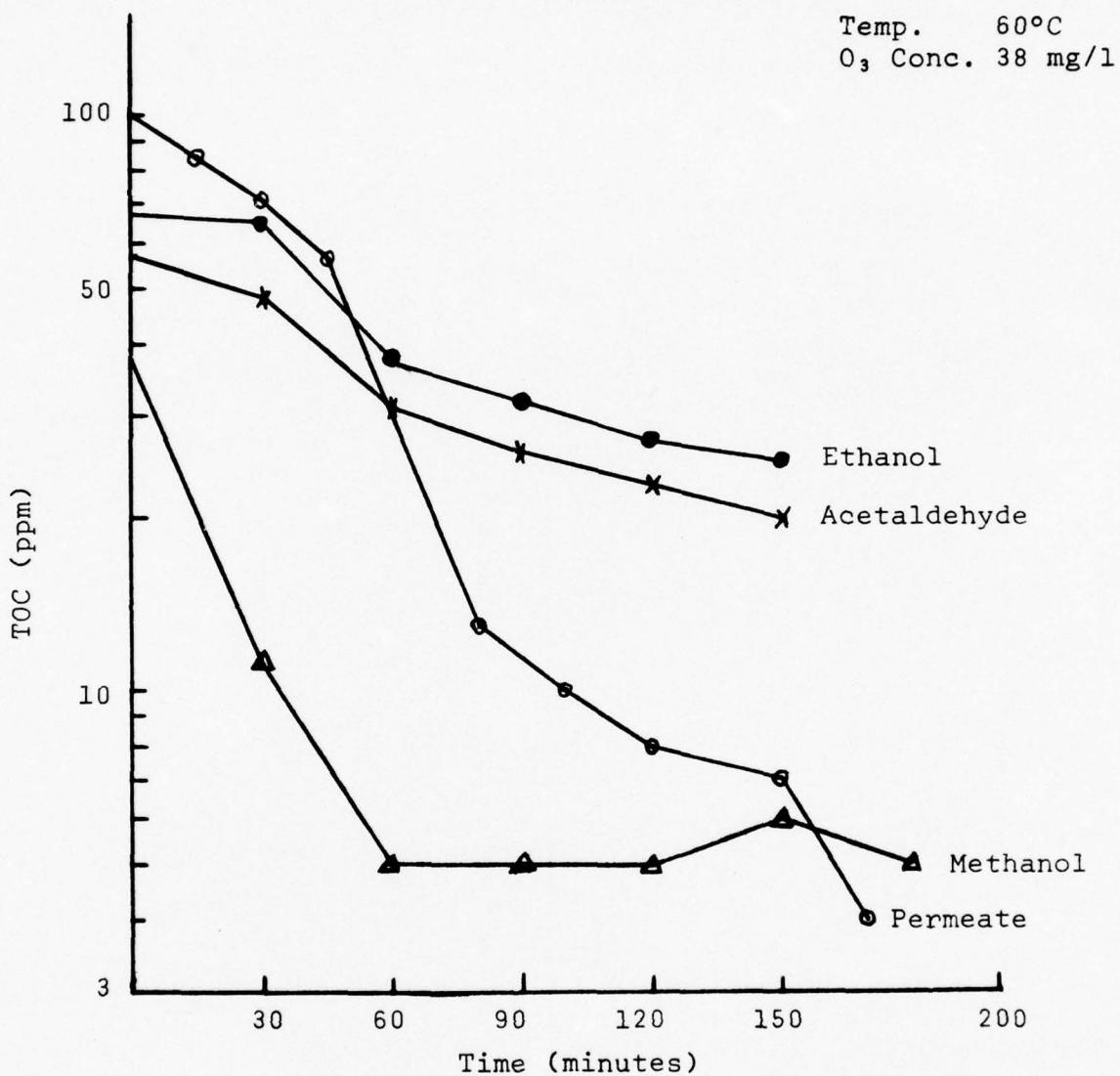
TOC REDUCTION OF MUST PERMEATE (X-RAY WASTE)
AT pH 6.5 AND A 100 PPM ACETALDEHYDE SOLUTION,
A 100 PPM ETHANOL SOLUTION
AND A 100 PPM METHANOL SOLUTION
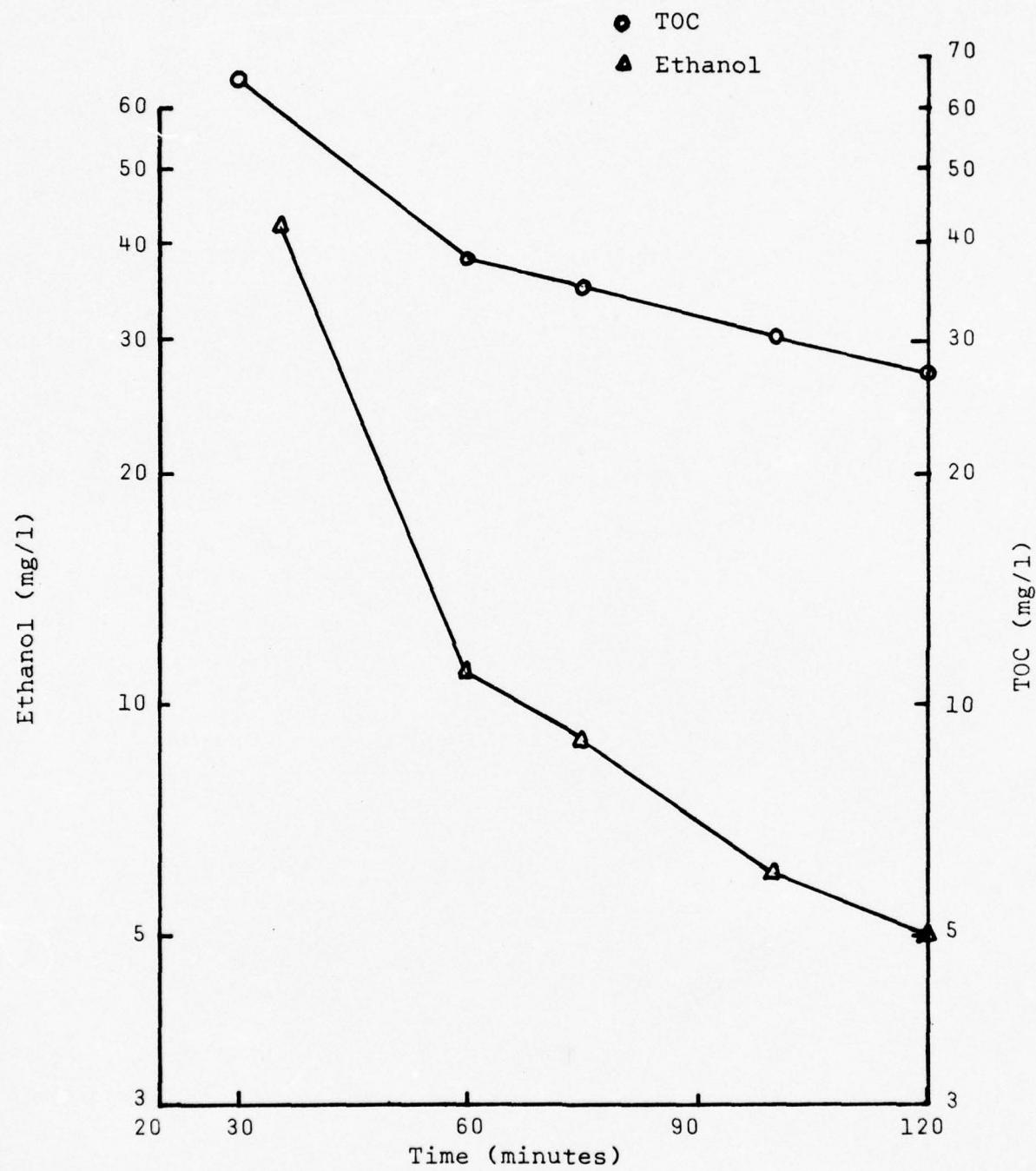
FIGURE 6

DETERMINATION OF RESIDUAL ETHANOL WITH DICHROMATE
METHOD AFTER OZONATION

α = activity coefficient for acetaldehyde in water at infinite dilution and $60^{\circ}C$

P^{o} = vapor pressure of acetaldehyde at $60^{\circ}C$, atm

π = atmospheric pressure, atm

t = time, minutes

For the acetaldehyde ozonation, $G \approx 0.021$ g/moles/min., $V = 55.5$ g moles, $\alpha \simeq 4.75$ $\frac{P^{o}}{\pi} = 4.05$, and ln $(x_i/x_t) = .0073t$.

As may be seen from Figure 7, the disappearance of acetaldehyde may be accounted for entirely by stripping.

For ethyl alcohol, however, the volatilization (gas stripping) rate is given by the equation:

$$\ln x_i/x_t = .0076t$$

As may be seen in Figure 8, gas stripping makes only a very minor contribution to the disappearance of ethanol.

For formaldehyde, the very low activity coefficient in aqueous solution[8] more than compensates for the high vapor pressure of the pure material, so that gas stripping contributes negligibly to its loss during ozonation.

Potassium permanganate is a strong oxidizing agent affecting many organic compounds in acid, neutral, or basic solution. During preliminary investigations, it was found that raw and treated MUST waste water when added to a roughly 100 ppm basic potassium permanganate solution effected a noticeable change in the deeply purple color. Aldehydes are known to be oxidized in basic potassium permanganate and when roughly stoichiometric amounts of potassium permanganate and acetaldehyde were allowed to react in basic solution at room temperature, a noticeable color change occurred in less than ten minutes. The results of these preliminary experiments were encouraging enough to warrant investigation into a colorimeter monitor for ozonated MUST product water based on permanganate oxidation of residual contaminants.

FIGURE 7

OZONATION OF ACETALDEHYDE AT 60°C

Liquid Volume = 1 liter
Oxygen Flow Rate = 0.5 l/min.
Ozone Concentration in Oxygen = 38 mg/l

$\ln x_i/x_t = .0077\ t$
(Rate of disappearance predicted by stripping)

TOC

TIME (minutes)

$$\ln x_i / x_t = .0076 \ t$$

(Rate of volatilization by gas stripping)

ppm Ethanol

FIGURE 8

OZONATION OF ETHANOL

(Ethanol concentration determined
spectrophotometrically after reaction
with dichromate)

TIME (minutes)
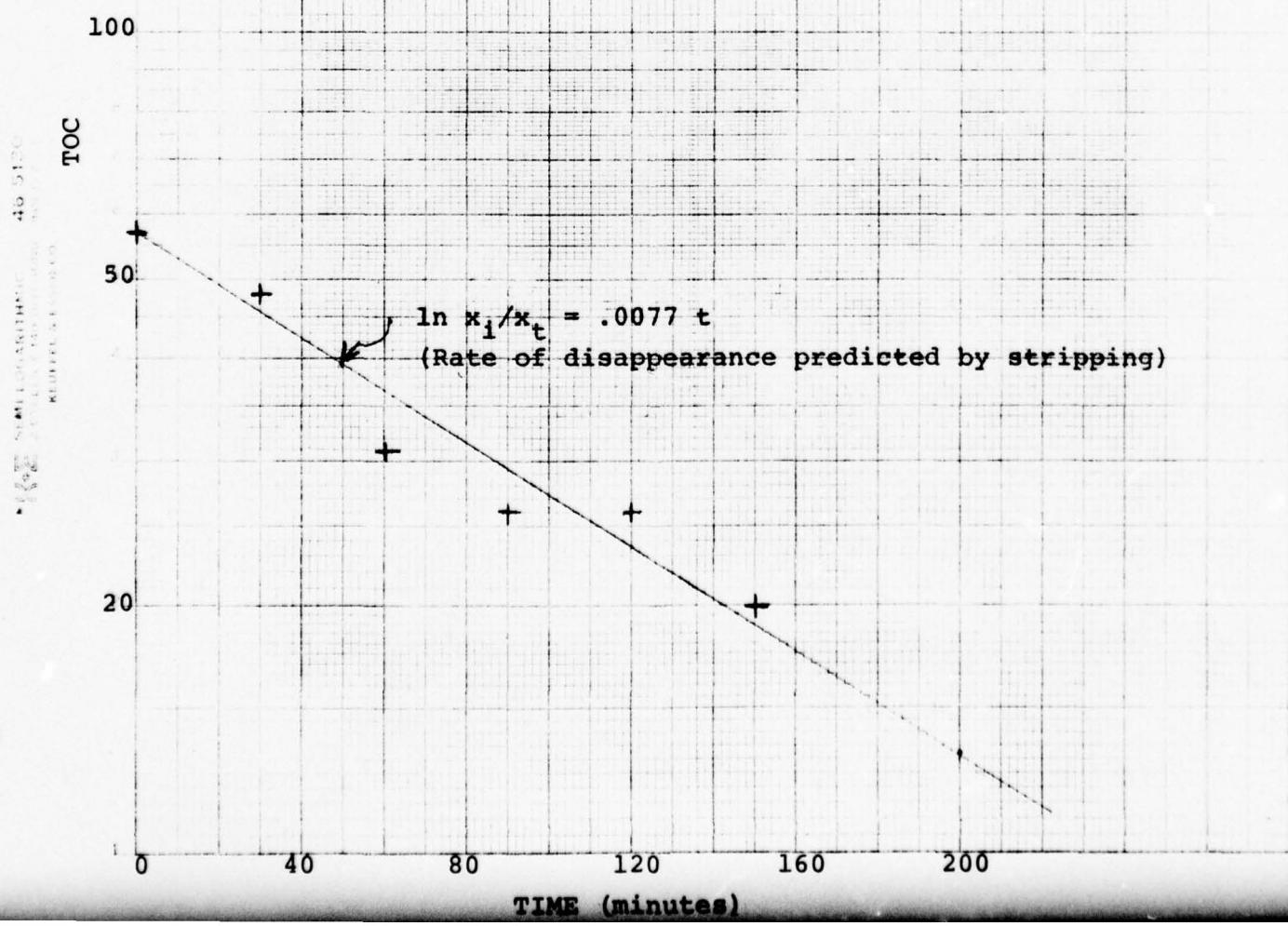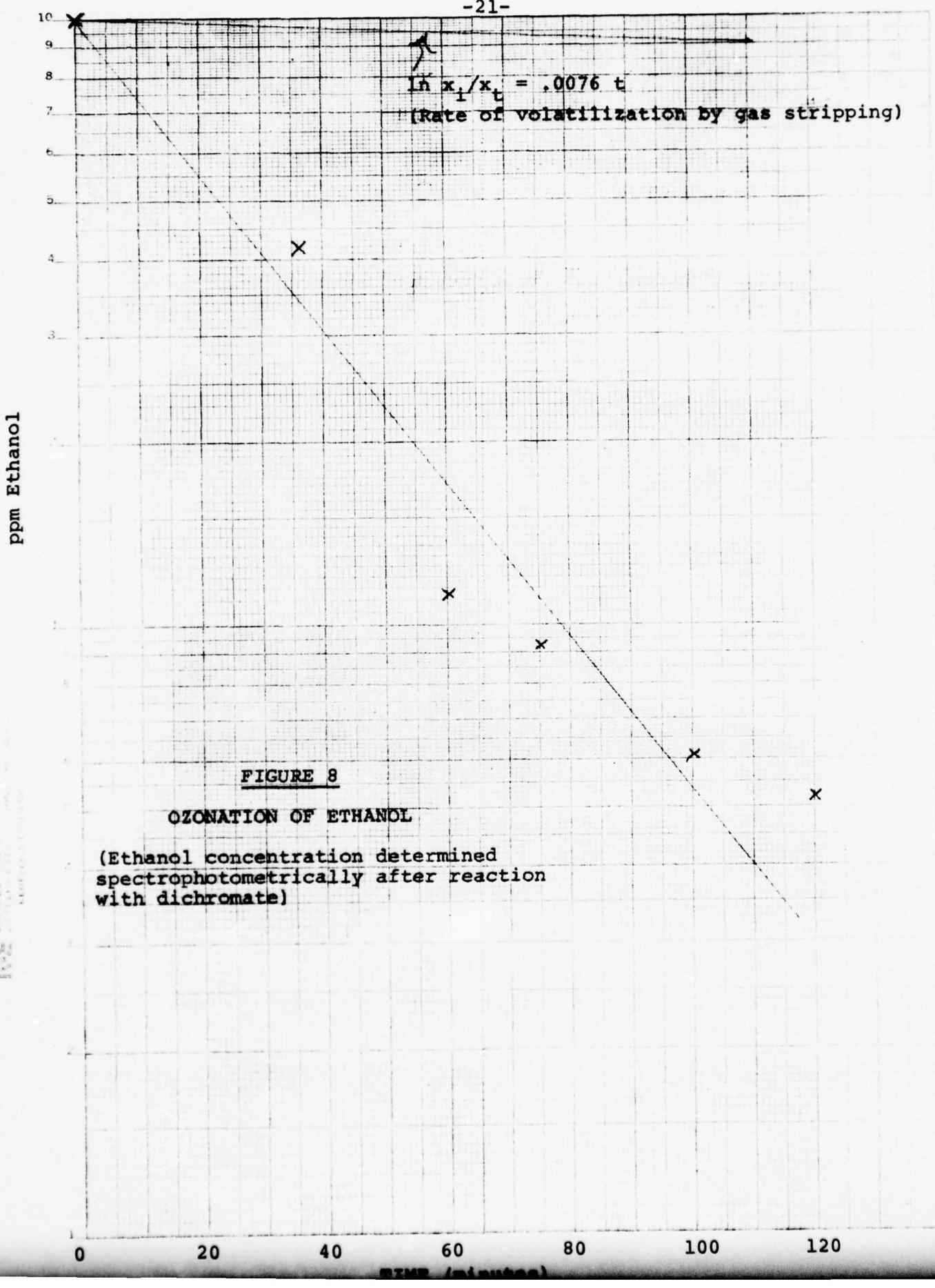
III.   MONITORING TECHNIQUES

   A.   Development of Acetaldehyde Assay Using Potassium
        Permanganate in Basic Solution

        A stock solution of 10,000 ppm acetaldehyde in dis-
        tilled water was prepared. Appropriate dilutions
        were made and samples of 5, 10, and 20 ppm were
        prepared. A slight excess of basic potassium per-
        manganate was added to the reaction flasks which
        were allowed to stand at room temperature for 20
        minutes. The total reaction volume of each flask
        was 5 ml and the pH was between 12 and 12.5. A
        blank was prepared in the same way using distilled
        water. The spectral absorption curve of each solu-
        tion was then determined using a Beckman 505 Scanning
        Spectrophotometer. For all measurements, the
        reference cell contained a solution of potassium
        hydroxide with a pH of approximately 12. The solu-
        tions were scanned from 200 nm to 600 nm. Figure
        9 shows the absorption spectrum of the various
        samples. From the spectra, it is obvious that
        suitable wavelengths for measurements of permanganate
        and manganate concentrations in a solution are 522
        and 426 nm, consistent with literature findings[6].
        The absorption at the former wavelength is due mainly
        to permanganate and at the latter mainly due to
        manganate.

        If permanganate ion is reduced no further than
        manganate ion, the ratio of the decrease in optical
        density at 522 nm to the increase in optical density
        at 426 nm may be shown to be:

        $$\frac{(\Delta\ OD)_{522}}{(\Delta\ OD)_{426}} = 11.54$$

        From Figure 9 it is clear that the Δ OD ratio experi-
        mentally observed is less. For 5 ppm acetaldehyde,
        the experimental ratio is 1.28; for 10 ppm, it is
        1.23; and for 20 ppm, it is 1.12. Since acetaldehyde
        and its oxidation products should have negligible
        absorption at 522 nm and 426 nm, and since reduc-
        tion of permanganate to manganese dioxide is likely
        to occur, the observed discrepancy is doubtless
        attributable to the production of colloidal manganese
        dioxide. Typically the size of colloidal manganese
        dioxide particles produced will be of the order of
        the wavelength of light[4]. The scattering effect
        is likely to be greater at the shorter wavelength

ABSORBANCE

FIGURE 9

ABSORPTION SPECTRUM OF KMnO$_4$ IN
BASIC SOLUTION REACTING WITH
VARIOUS CONCENTRATIONS OF CH$_3$CHO

λ (nm)
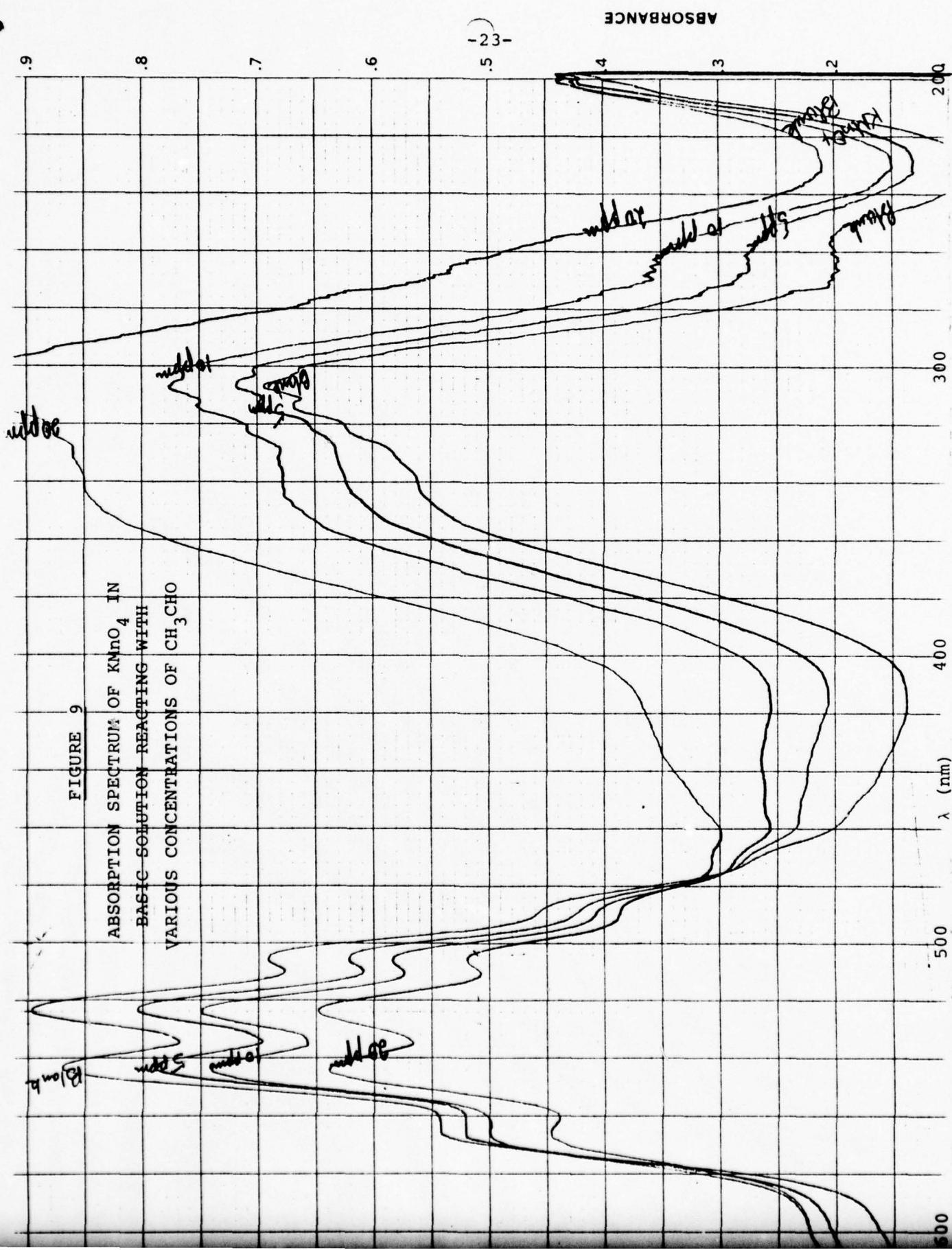
so that a relatively small ratio of manganese
dioxide to manganate ion could account for the
discrepancy in Δ OD ratios. The formation of
manganese dioxide can be suppressed by increasing
the concentration of base and maintaining a
sufficient excess of permanganate ion (see later
discussion and Figures 13, 14, and 15).

Calibration curves, which show the disappearance
of permanganate at 522 nm or the appearance of
manganate at 426 nm for a given temperature as a
function of ppm of acetaldehyde, should be adequate
for estimation of acetaldehyde concentration in
solution provided adequate time is allowed for com-
pletion of the reaction. Thus, the next step was
to investigate the reaction at 522 nm and 426 nm
and to determine optimum time and temperature for
the reaction.

Stoichiometric requirements for permanganate oxida-
tion of aldehydes in alkaline solution are not clear
because oxidation to the corresponding carboxylic
acid competes with carbon-carbon bond scission[6].
Oxidation to the corresponding carboxylic acid in
alkaline solution requires 2 moles of permanganate
per mole of aldehyde, as indicated in Equation 1,
while carbon-carbon bond cleavage can consume many
more moles of permanganate per mole of aldehyde[6].

$$CH_3COH + 2\ MnO_4^- + 2\ OH^- = CH_3COOH + 2\ MnO_4^= + H_2O \qquad (1)$$
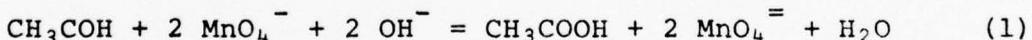
The U. S. Army Medical Research and Development
Command has established as an interim standard, a
TOC level of 5 ppm as the maximum acceptable for
treated MUST waste water reuse. The acetaldehyde
concentration in the treated MUST waste water must,
therefore, be less than 10 ppm since this corresponds
to a TOC of 5 ppm, presuming no other compounds
present. As treatment processes are improved and
optimized, the acceptable TOC level will eventually
be reduced further. The range of the calibration
curve for an acetaldehyde assay was therefore
selected as from 1-10 ppm. Based upon reaction (1)
above, the stoichiometric amount of $KMnO_4$ to react
with 10 ppm of CH_3COH is 72 ppm. A solution A was
prepared in the following way: 1 ml of ($KMnO_4$)
solution containing 7200 mg/liter plus 4 ml distilled
water plus 5 ml 1 MKOH solution were added to a
reagent flask. The final $KMnO_4$ concentration of
this solution is 720 mg/l. Since $KMnO_4$ undergoes
slight decomposition in basic solution, reagent A
has to be prepared freshly before each test. To

3 ml of distilled water (for blank) 0.3 ml of solution A was added. This gave a final $KMnO_4$ reaction concentration of 65.4 mg/liter and a pH of 12.2. The reaction was followed spectrophotometrically at 522 nm and OD readings were recorded at two-minute intervals. This procedure was repeated with 1, 5, and 10 ppm acetaldehyde solutions replacing the distilled water. As mentioned above, at 522 nm the disappearance of permanganate is measured. The entire procedure was then repeated but this time the measuring wavelength of the spectrophotometer was set at 426 nm and the appearance of manganate was determined. The results of these experiments are shown in Figures 10 and 11. The reactions at both wavelengths were followed over a period of one hour. In Figures 10 and 11, the results were plotted up to 20 minutes since the curves were fairly straight from that point onwards after the blank values were subtracted. It is also evident from the two figures that the curves reach a near maximum level at different times; when observed at 522 nm, it is about six minutes and at 426 nm, it is about ten minutes. The longer time to reach equilibrium at 426 nm is probably due to the kinetics of formation and growth of colloidal manganese dioxide particles. These particles are likely to scatter light more at 426 nm than at 522 nm. As short as possible a reaction time is essential so that variations of acetaldehyde levels in the processed effluent stream can be detected quickly.

Advantages of monitoring the 522 nm wavelength are the shorter time to a constant reading and the higher extinction coefficient for the permanganate ion. Advantages of monitoring the 426 nm wavelength are the possibly higher sensitivity of the colorimeter in the low OD range and the additional Δ O.D. resulting from manganese dioxide production, provided the effect is reproducible.

Standard curves were obtained at both 522 nm and at 426 nm, with the 522 nm readings taken after six minutes at room temperature for reaction, and those at 426 nm taken after 20 minutes. These curves are presented in Figure 12. Additional data were obtained using a Cary 14 Recording Spectrophotometer to study the effect of base concentration on the OD readings and on permanganate decomposition. An increase in base level should make manganese dioxide less likely to form but should accelerate the slow

FIGURE 10: REACTION BETWEEN $KMnO_4$ AND CH_3COH IN BASIC SOLUTION

Final $[KMnO_4]$ = 65.4 mg/l
Final pH 12.2
λ 522 nm
O.D. values corrected for blanks (Blank - Reading)
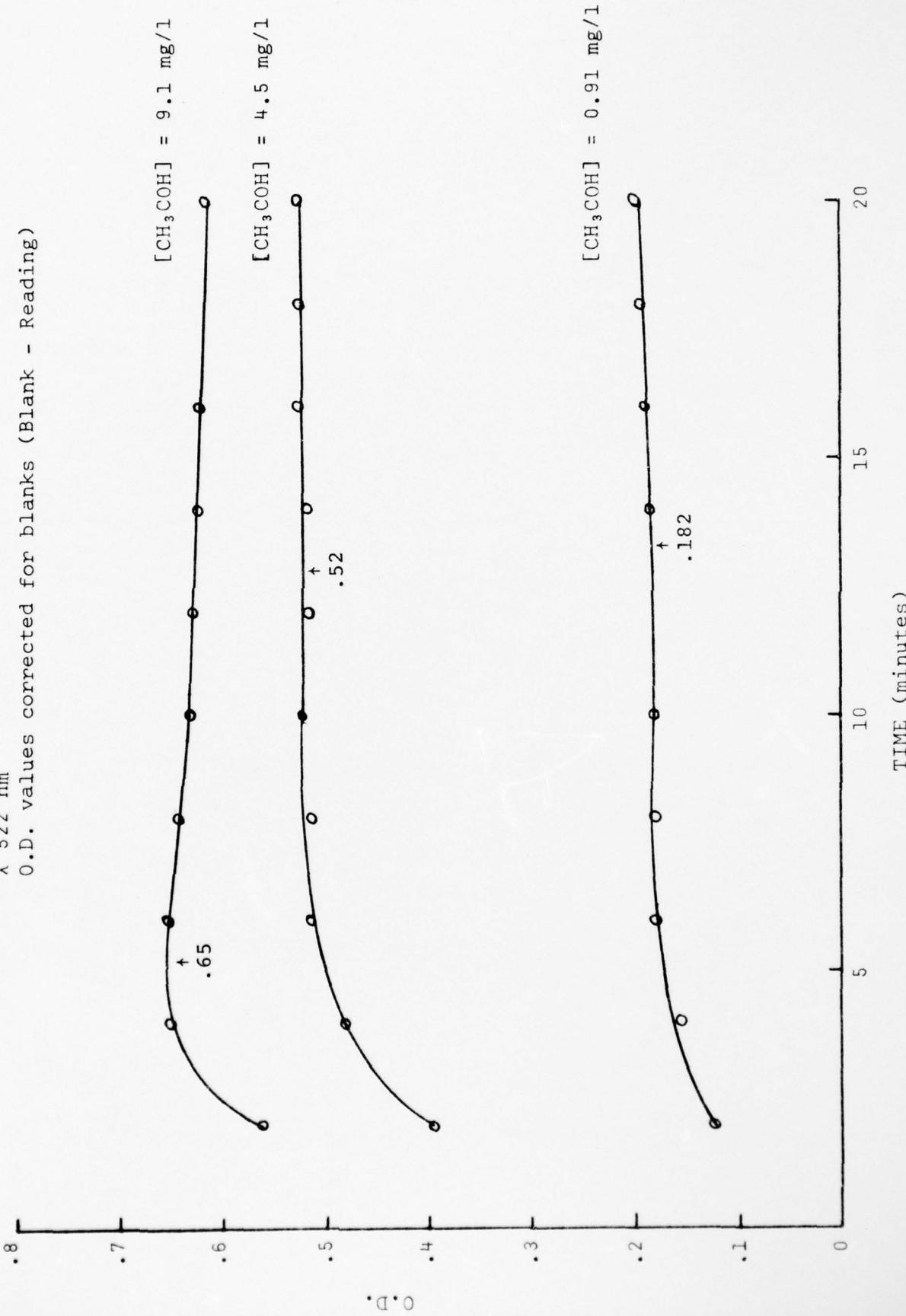
FIGURE 11: REACTION BETWEEN KMnO₄ AND CH₃COH IN BASIC SOLUTION

Final [KMnO₄] = 65.4 mg/l
Final pH 12.2
λ 426 nm
O.D. values were corrected for blanks (Reading - Blank)
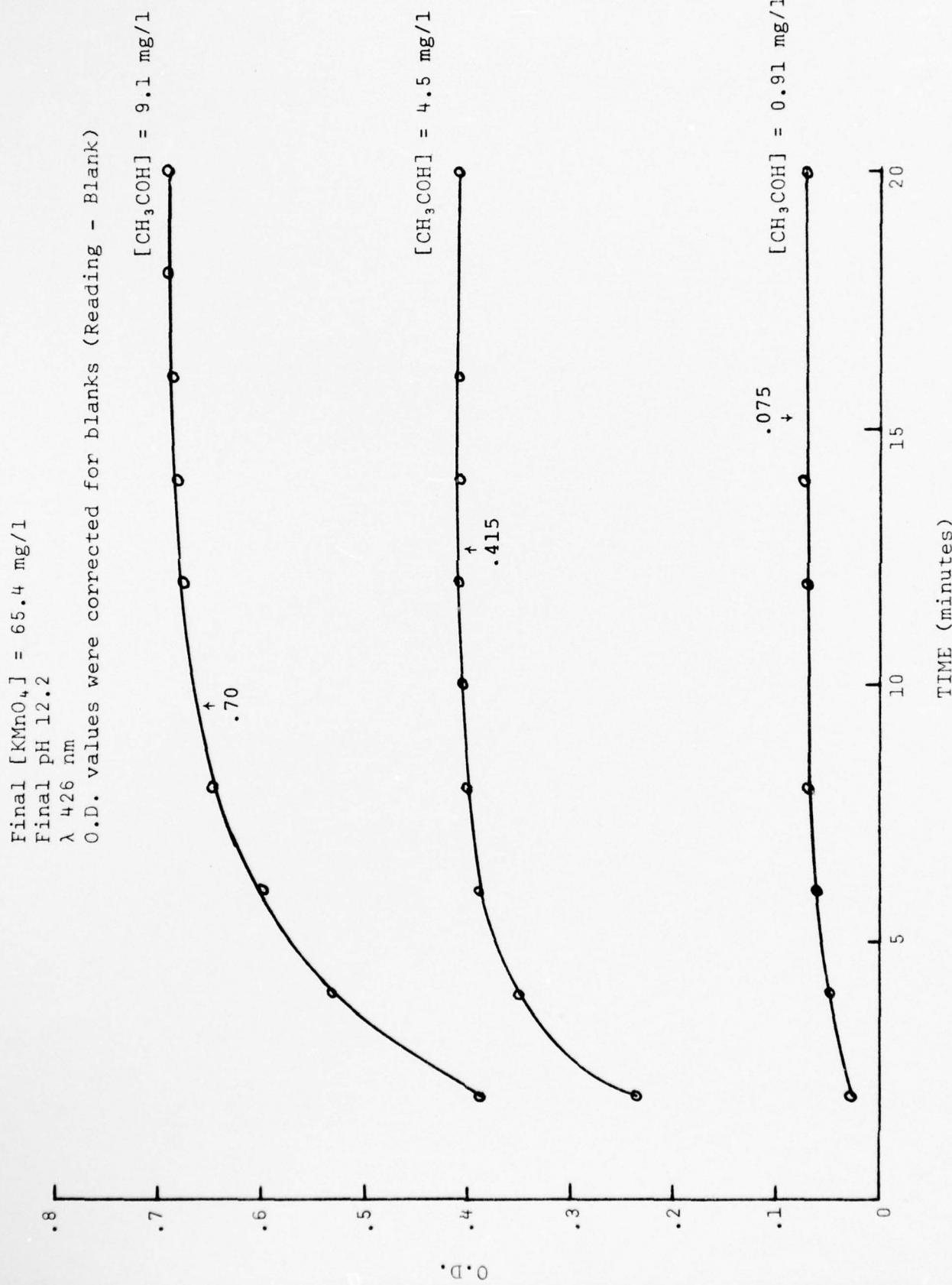
FIGURE 12: STANDARD CURVE OF $KMnO_4$ VERSUS CH_3CHO IN BASIC SOLUTION

Final $(KMnO_4)$ = 65.4 mg/l
pH 12.5
Room Temperature
O.D. values corrected for blank

λ 426 nm read at 20 min. (reading-blank)

λ 522 nm read at 6 min. (blank-reading)
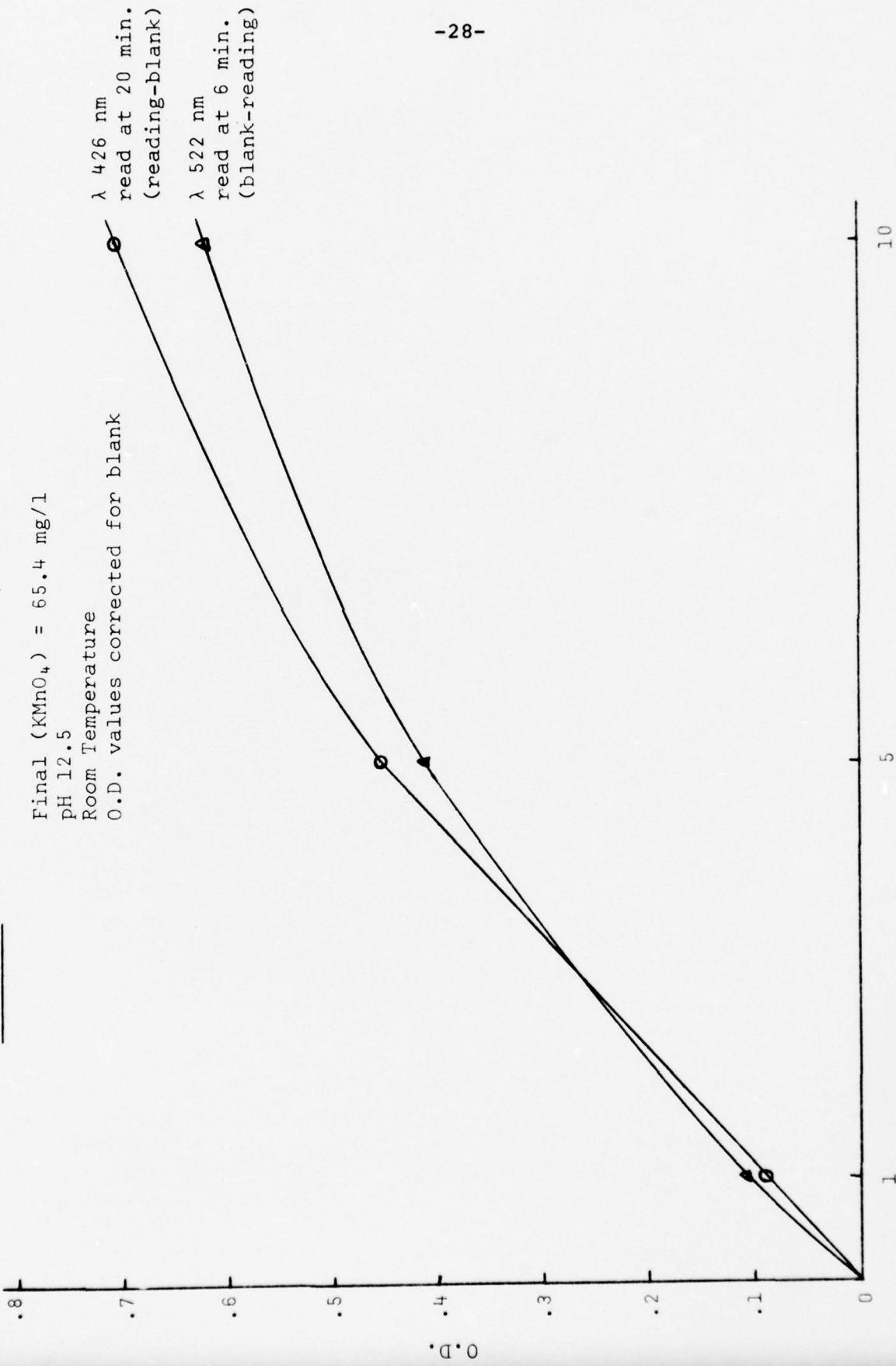
autodecomposition of permanganate. Results are presented in Figures 13, 14, and 15 and Table 0. A higher base concentration does result in slightly more reaction and in a higher $\Delta OD_{522}/\Delta OD_{426}$ ratio and is, therefore, helpful in suppressing manganese dioxide formation. It has negligible effect on permanganate decomposition kinetics for the time scale of interest. A higher base concentration is therefore desirable.

From Figure 14 the moles of permanganate which react with a mole of acetaldehyde may be estimated to be at least 2.8. The true number is somewhat higher because the manganese dioxide scattering at 522 nm raises the OD and therefore makes the permanganate disappearance appear to be smaller than it is.

B. Preliminary Design Work on a Continuous Flow Monitoring Technique

Permanganate oxidation of acetaldehyde appears to meet the requirements for a continuous monitoring technique. If necessary, ethanol or acetaldehyde may be added continuously into the process stream upstream of the ozonation reactor in an appropriate concentration and acetaldehyde monitored continuously in the effluent stream. Permanganate will also oxidize ethanol, although more slowly; if ethanol is added as a tracer, the amount of tracer utilized and the permanganate oxidation conditions must be selected so as to guarantee tripping of the system alarm should the ozonation reactor be malfunctioning so as not even to oxidize ethanol to acetaldehyde.

One schematic for a permanganate colorimeter monitor is shown in Figure 16. $KMnO_4$ and KOH are stored in separate tanks. Originally distilled water and RO permeate are also stored in tanks but once the system is on line, RO permeate is fed to the monitor via a direct line from the processed effluent stream and distilled water is produced by an appropriate unit on a continuous basis. The reagents are fed into two Vortex mixers with volumes of about one ml and tangental inlets into the mixing chambers. From the Vortex mixers the reaction mixture enters static mixers and coils of appropriate holdup to give the desired residence time for reaction. The length of the coils is chosen to allow adequate reaction time; from Figure 10, a residence time of about six minutes is desirable. From the coils, the reaction mixture enters flow-through cells of a double beam colorimeter where the difference in optical density between the two streams is determined. The reaction mixture of the sample stream consists

FIGURE 13: KMnO$_4$ REACTION WITH CH$_3$CHO IN BASIC SOLUTION FOR 10 MINUTES @ 21°C AS A FUNCTION OF WAVELENGTH AND {OH} CONCENTRATION

{KMnO$_4$} = 36 mg/l

{OH$^-$} = 0.025 M

pH = 12.24

λ522 nm

λ426 nm

Acetaldehyde Concentration, mg/l

{KMnO$_4$} = 36 mg/l

{OH$^-$} = 0.1 M

pH = 12.88

λ522 nm
λ426 nm

Acetaldehyde Concentration, mg/l
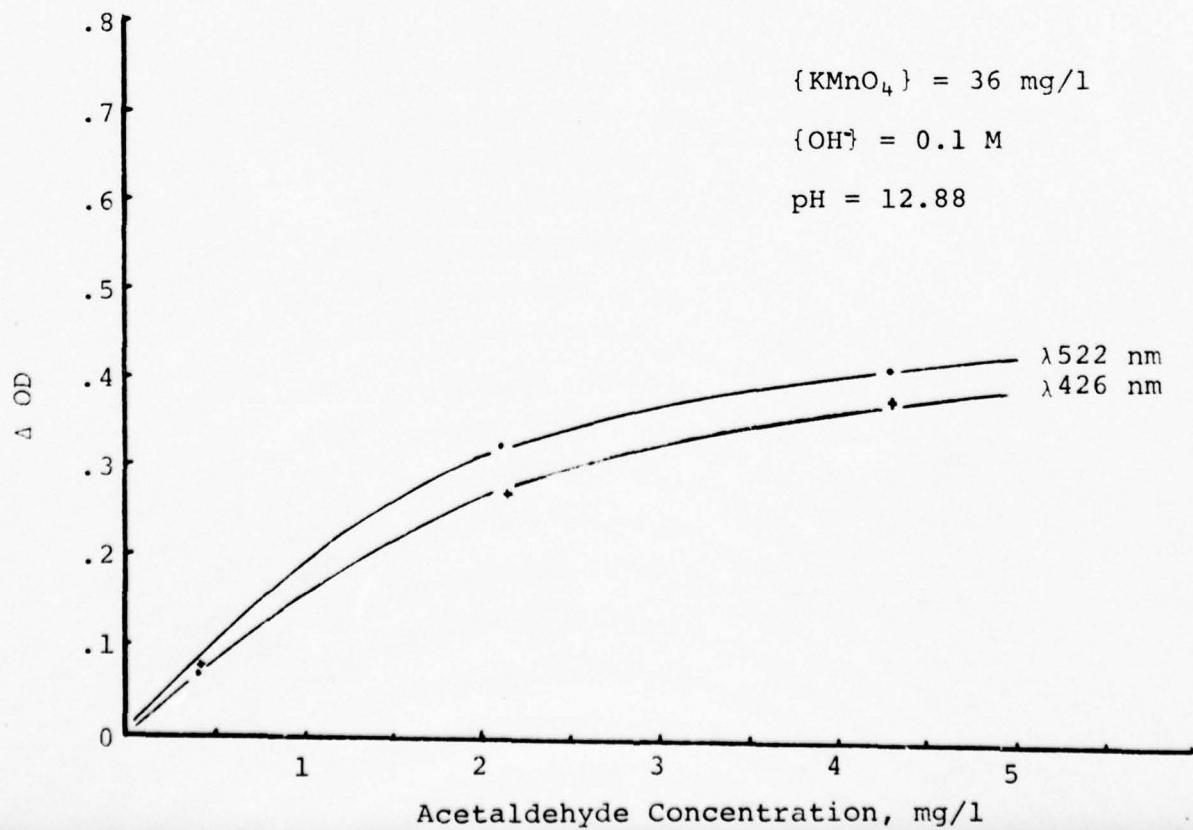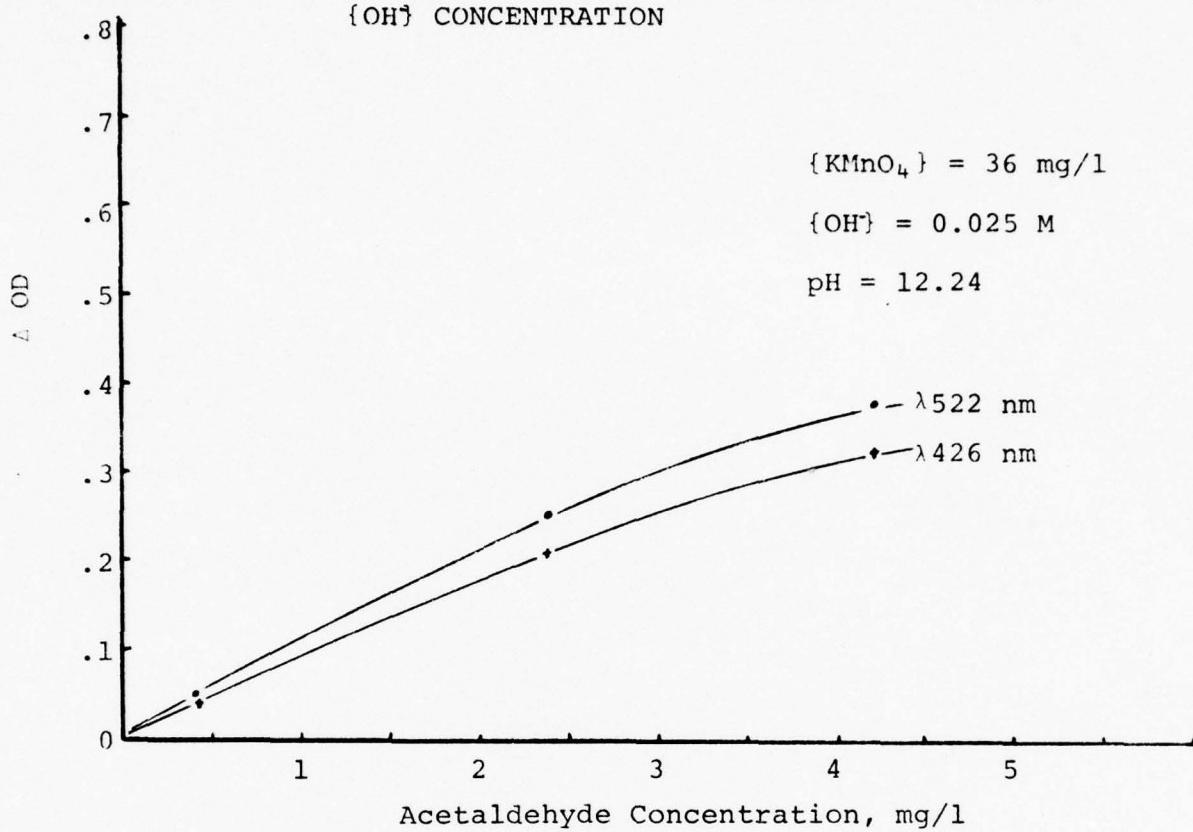
FIGURE 14: $KMnO_4$ REACTION WITH CH_3CHO IN BASIC SOLUTION
FOR 10 MINUTES AT $21^{\circ}C$ AS A FUNCTION OF WAVELENGTH
AND {OH} CONCENTRATION

$\{KMnO_4\}$ = 36 mg/l

$\{OH\}$ = 0.2 M

pH = 13.13
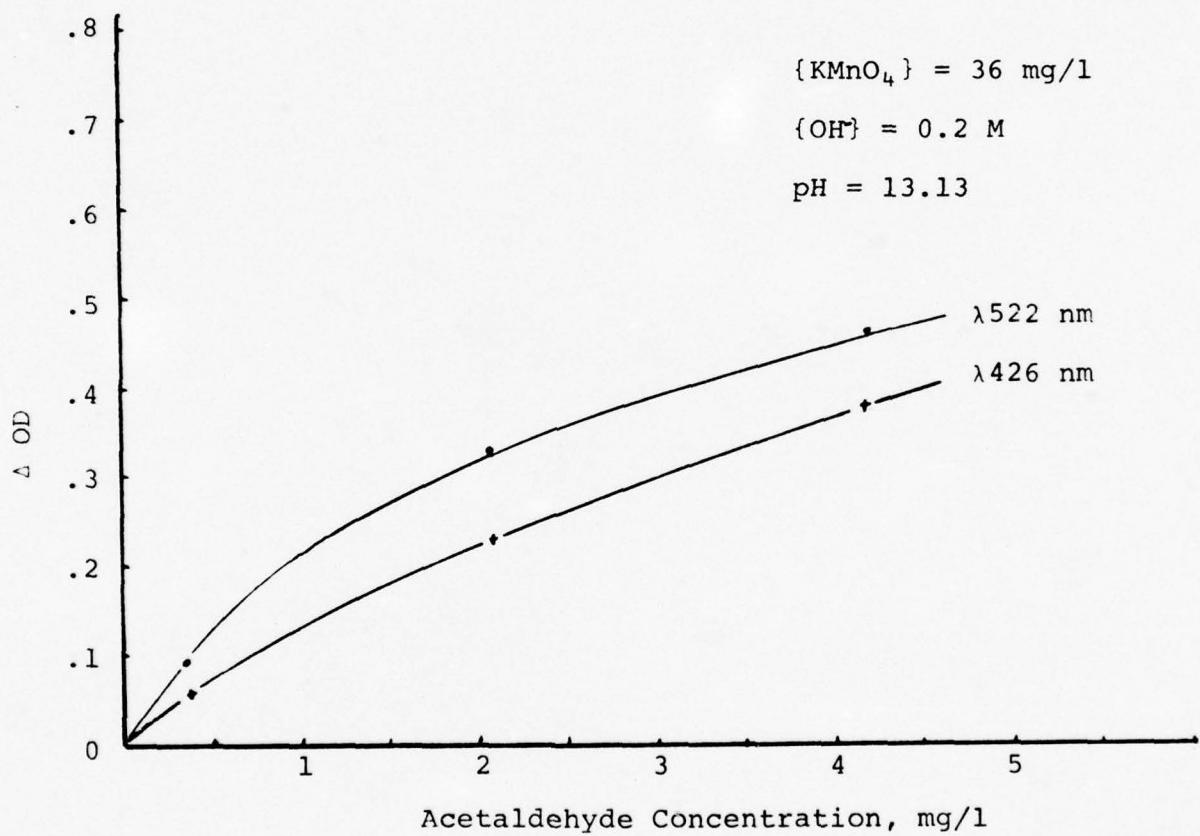
FIGURE 15: KMnO$_4$ DECOMPOSITION IN BASIC SOLUTION AT ROOM TEMPERATURE

λ522 nm

{KMnO$_4$} = 36 mg/l

{OH} = Parameter

λ426 nm

{KMnO$_4$} = 36 mg/l

{OH} = Parameter
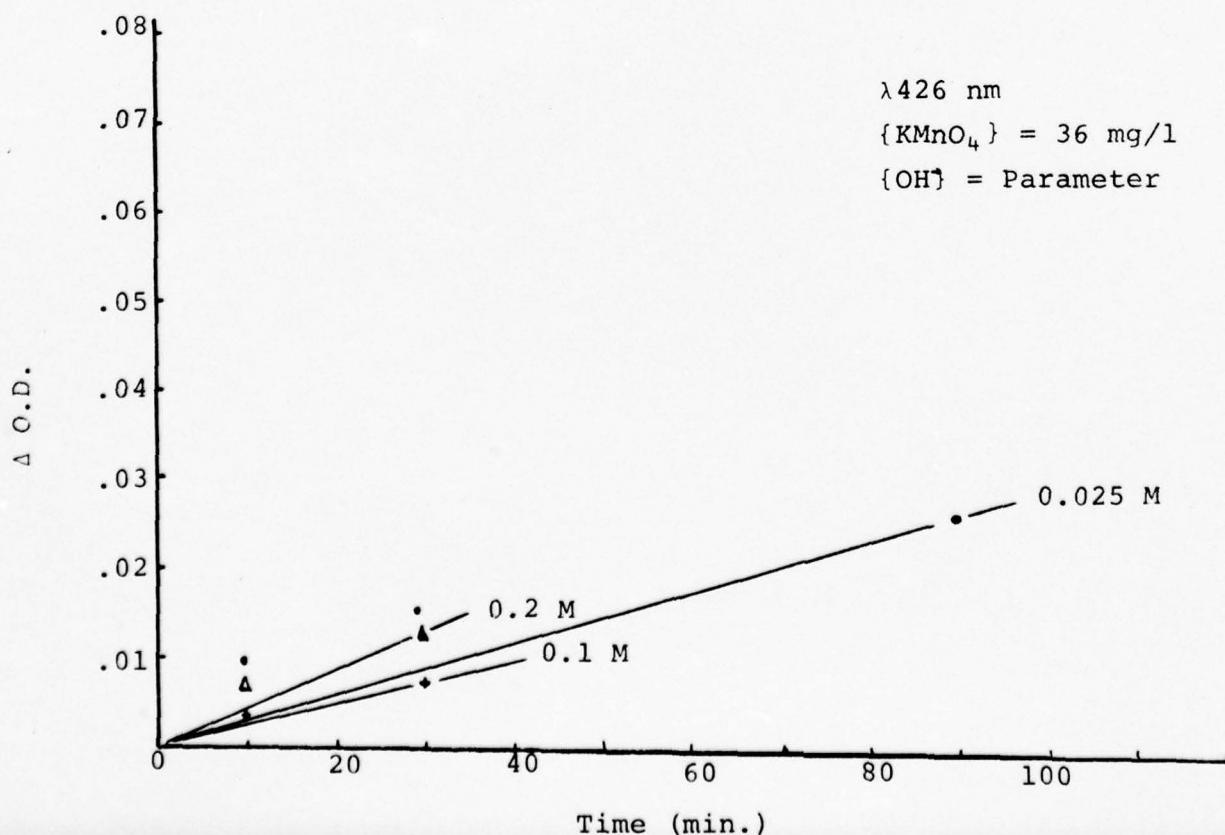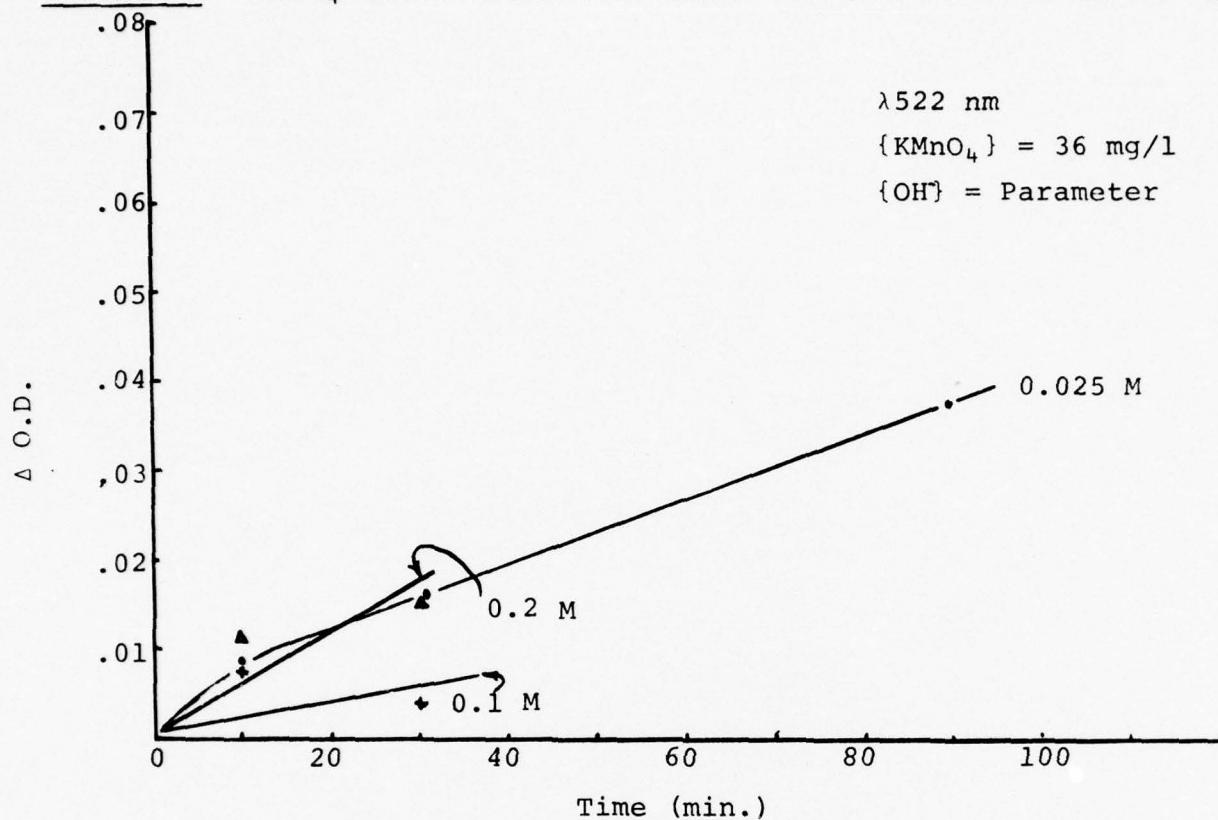
TABLE 0

20 HOUR Δ OD OF $KMnO_4$ DECOMPOSITION AS A
FUNCTION OF {OH} AT WAVELENGTHS OF 426 AND 522 nm

{OH}	λ426 nm	λ522 nm
0.0 M	0.026	0.006
0.025 M	0.120	0.025

FIGURE 16

SCHEMATIC OF PERMANGANATE COLORIMETER MONITOR
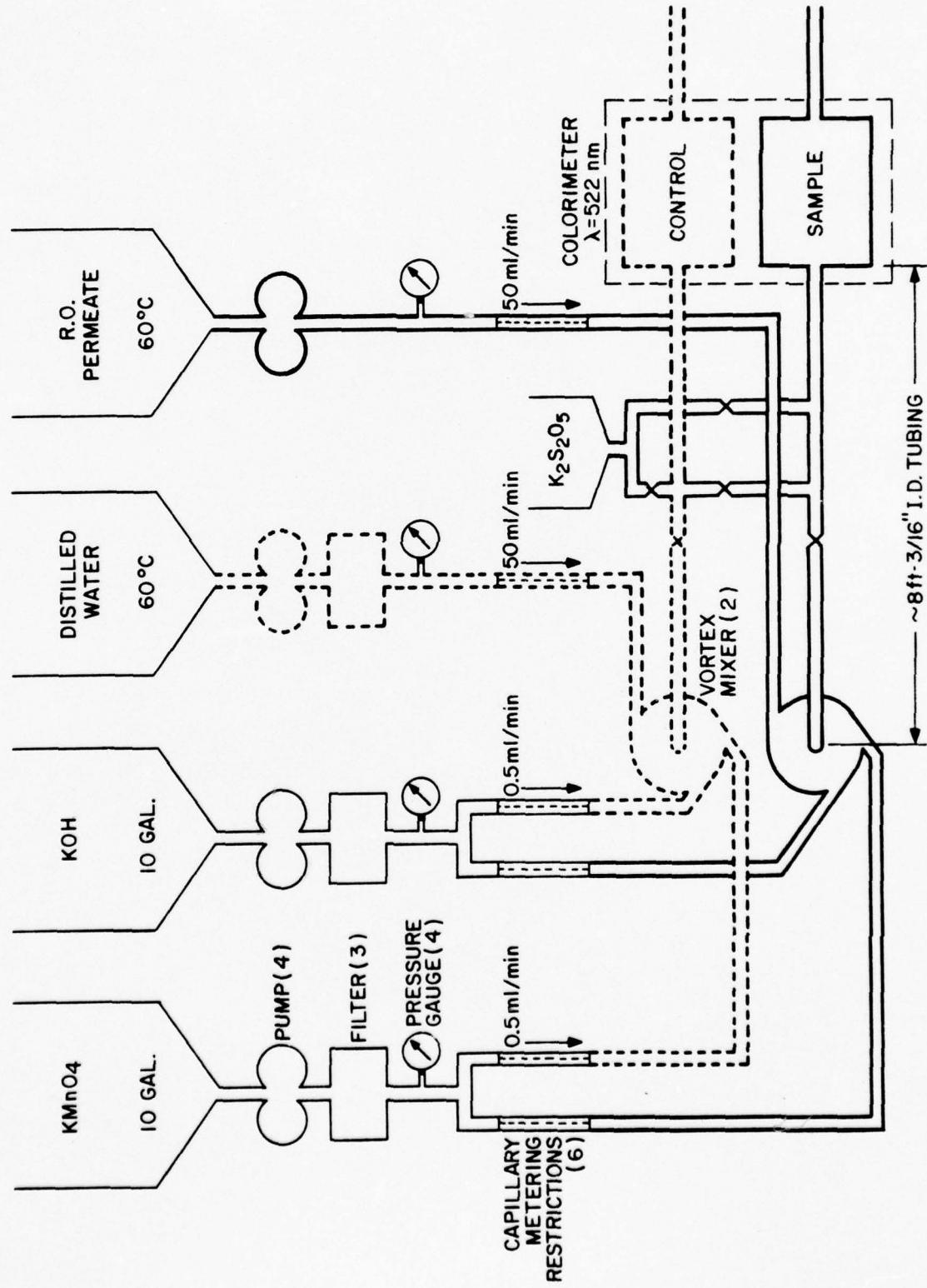
of $KMnO_4$, KOH and RO effluent whereas the reference stream contains $KMnO_4$, KOH, and distilled water.

The colorimeter compares the disappearance of permanganate ion in ozonated MUST RO permeate, to which potassium permanganate has been added, with the permanganate ion concentration in a distilled water sample, to which an identical quantity of permanganate solution has been added.

A second schematic for a permanganate colorimeter monitor is shown in Figure 17. MUST product water to which permanganate and base have been added is fed to the colorimeter cells in series. The mixture is fed to the first cell immediately after mixing; then flows through a coil of suitable holdup to allow time for the permanganate oxidation to occur; and then flows through the second colorimeter cell. The residence time between the mixing of the permanganate and base with the product water and the flow of this solution through the first colorimeter cell is kept sufficiently short that relatively little reaction occurs during this time. This first cell can then serve as a reference cell and indicate the concentration of permanganate prior to reaction while the second cell indicates the permanganate concentration after reaction.

A third schematic for a permanganate colorimeter is shown in Figure 18. A colorimeter with a single cell is used and the absorbance at two wavelengths is monitored. MUST Product water to which permanganate and base have been added and which has flowed through a delay coil which provides the requisite residence time for reaction to occur, flows through the cell. One of the monitoring wavelengths is 522 nm to monitor the disappearance of permanganate as a result of reaction. The second wavelength may be chosen at an isosbestic point where the absorbance of permanganate and manganate ions are equal; the absorbance of the cell at this wavelength will then be independent of the relative concentrations of these two ions but will vary directly as the sum of their concentrations. The absorbance at this second wavelength then provides the requisite information on the concentration of permanganate added which is provided by the reference cell in the two previously discussed colorimeter schematics.

Alternatively, the two wavelengths may be chosen to be 522 nm and 426 nm, with the ratio of transmittances at these wavelengths the monitoring output. For low contaminant levels, the ratio $\dfrac{OD_{426}}{OD_{522}}$ will be

FIGURE 17

MONITOR SCHEMATIC

The KMnO$_4$ and KOH solutions and the distilled water were nitrogen pressurized at ~14.2 psi. The pressure on the MUST water feed was ~13.0 psi.
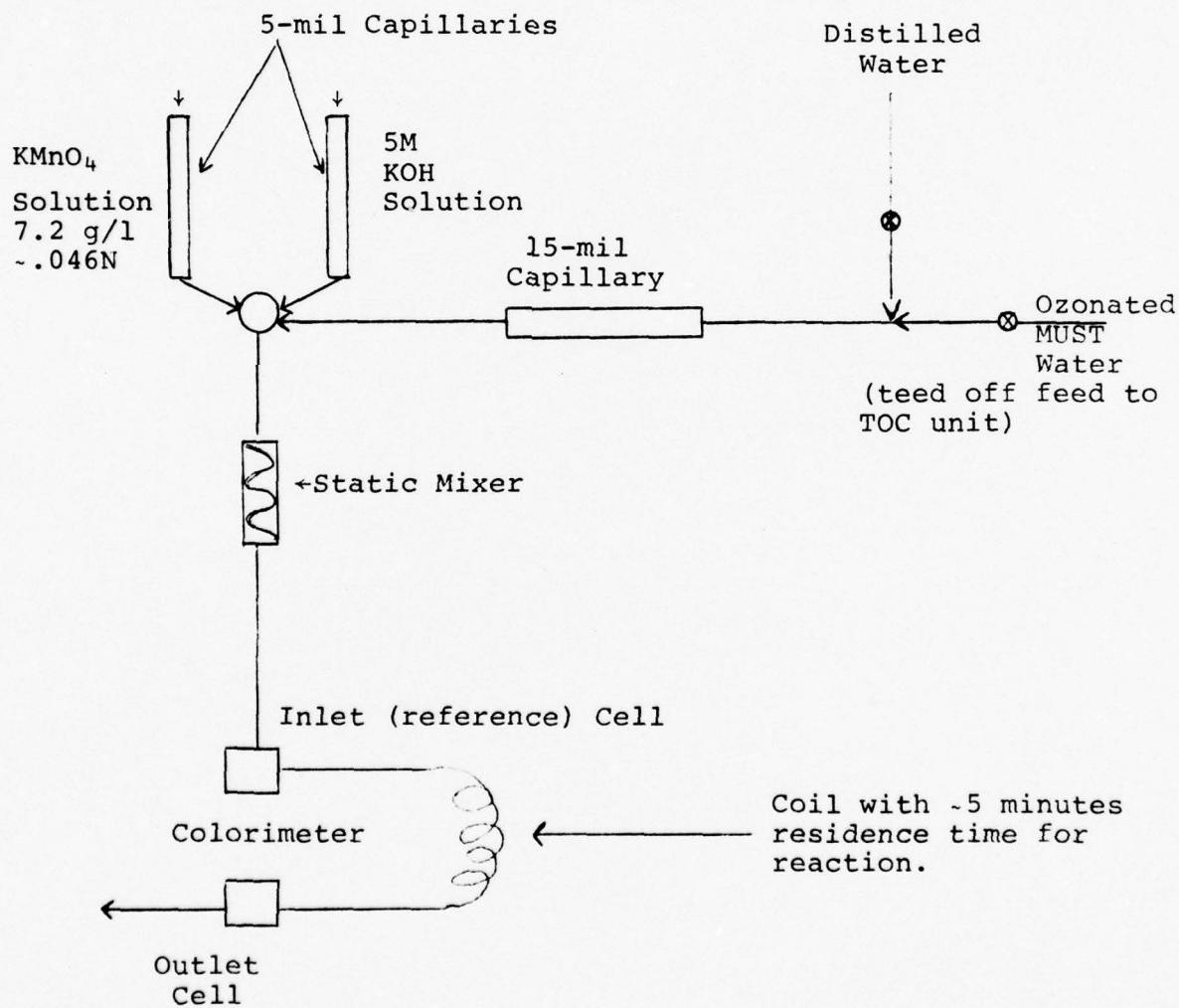
Colorimeter monitoring transmission at 522 nm

FIGURE 18

DUAL WAVELENGTH MODE OF OPERATION
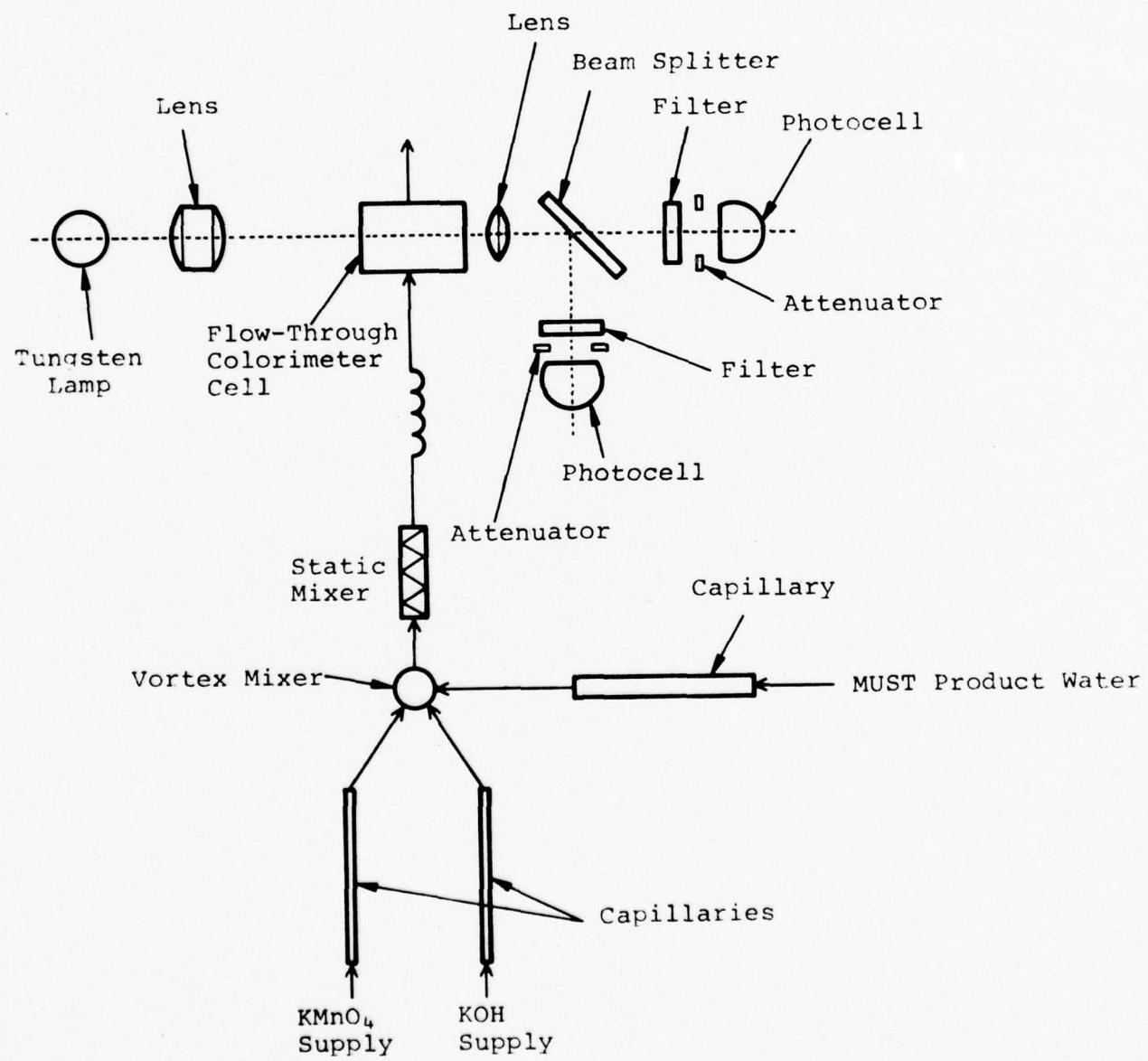
low and for high contaminant ratios, it will be
high. One advantage of using these two wavelengths
is that for a given contaminant level, they will
produce a larger instrument reading than the other
approaches. A second advantage is that the ratio
will be relatively insensitive to fluctuations in
permanganate concentration at low contaminant levels
since these will have little effect on the numerator
(OD_{426}).

The response of the monitor as the concentration of
impurities which are oxidizable by permanganate
varies may be analyzed as follows:

$$D_{522} = 2370 \, \{MnO_4^-\} + 387 \, \{MnO_4^{2-}\}$$

$$D_{426} = 77 \, \{MnO_4^-\} + 1370 \, \{MnO_4^{2-}\}$$

$$D_{isosbestic} = c \, (\{MnO_4^-\} + \{MnO_4^{2-}\})$$

where

D_{522} = optical density at 522 nanometers

$D_{isosbestic}$ = optical density at an isobestic point

D_{426} = optical density at 426 nanometers

$\{MnO_4^-\}$ = molarity of permanganate ion

$\{MnO_4^{2-}\}$ = molarity of manganate ion

and the coefficients are the extinction coefficients
for the respective ions and wavelengths.

From the definition of optical density

$$I_{522} = I_{o_{522}} \, e^{-D_{522}}$$

$$I_{426} = I_{426} \, e^{-D_{426}}$$

where I_o = light intensity incident on the colorimeter

I = transmitted light intensity.

For the two cell mode of operation, the colorimeter output is the log of the ratio of the transmitted light intensities through the two cells:

$$S_1 = \ln\left[\frac{I_{522_{DW,\ 5\ min}}}{I_{522_{WW,\ 5\ min}}}\right] = D_{522_{DW,\ 5\ min}} - D_{522_{WW,\ 5\ min}}$$

$$\text{and } S_2 = \ln\left[\frac{I_{522,\ WW_{\sim 30\ sec}}}{I_{522,\ WW_{\sim 5\ min}}}\right] = D_{522,\ WW_{30\ sec}} - D_{522,\ WW_{5\ min}}$$

where the subscript DW refers to distilled water;

the subscript WW refers to waste water;

the subscripts 30 sec and 5 min refer to the time allowed for permanganate reaction before monitoring transmittance;

S_1 refers to the colorimeter signal output with the mode of operation depicted in Figure 16;

S_2 refers to the colorimeter signal output with the mode of operation depicted in Figure 17.

Similarly for the single cell, dual wavelength mode of operation, the colorimeter output is the log of the ratio of the transmitted light intensities at the two wavelengths:

$$S_3 = \ln\left[\frac{I_{522}^{5 \text{ min}}}{I_{\text{Isosbestic}}^{5 \text{ min}}}\right] = D_{522}^{5 \text{ min}} - D_{\text{Isosbestic}}^{5 \text{ min}}$$

$$\text{and } S_4 = \ln\left[\frac{I_{522}^{5 \text{ min}}}{I_{426}^{5 \text{ min}}}\right] = D_{522}^{5 \text{ min}} - D_{426}^{5 \text{ min}}$$

$KMnO_4$ has a very high extinction coefficient and this reagent has to be added very accurately. Suitable micropumps are very expensive and of questionable accuracy and reliability and pose maintenance problems. For this reason, reagent dispensing is accomplished by the use of capillary metering restrictions with a pressure head to force the fluid through the capillaries. Using Poiseuille's Law, the dimensions of the capillaries to deliver a predetermined volume with a known pressure head can be calculated. To generate the necessary pressure, a separate pump for each line could be used as shown in Figure 10. A probably less-expensive method (also fewer moving parts) is to use a single nitrogen tank to pressurize the reagent dispensers and this approach was selected for initial development. The pressure necessary to force the liquid through the capillaries and deliver the required volume was kept relatively low, between 10 and 20 psi, so as to minimize problems generated by the dissolving of gas in the reagents. At higher pressures diaphragms would have to be used to separate the two media and prevent the dissolving of gas.

The diameters of the capillaries are very small and proper precautions must be taken to prevent blocking. An inexpensive method is to use fine filters to remove small particulate impurities. The filter material has to be inert to chemical attack by the reagents, i.e., $KMnO_4$ and KOH. Very fine mesh stainless steel clotch is used for this purpose. Pressure gauges indicate the proper flow or reagents through the system. The gauges are protected from chemical corrosion by stainless steel diaphragms. Eventually all tubing containing reagents as well as the Vortex mixers should be made of stainless steel.

Slow decomposition of $KMnO_4$ occurs, especially after
the Vortex mixer where the solution is made basic by
the addition of KOH. A fine, dark-brown film of
manganese dioxide deposits gradually on the surface
of the materials in contact with the reaction
mixture. The stainless steel tubing and the flow-
through cell of the colorimeter therefore require
periodic cleaning, particularly since the decompo-
sition reaction is autocatalytic, i.e., is catalyzed
by manganese dioxide. A 1% solution of sodium or
potassium bisulphite can remove all MnO_2 rapidly
by chemical reaction[4]. A reservoir containing
$K_2S_2O_5$ is connected to the monitor so the parts in
question may be flushed periodically whenever the
need arises as determined experimentally.

C. Abcor Pilot Run

The permanganate colorimeter monitor was set up at
the Abcor pilot plant late in August of 1974 to
operate in parallel with the Ionics TOC instrument
so as to determine its suitability for monitoring
the quality of MUST product water. The colorimeter
was set up to operate as shown in Figure 17; the
product water with permanganate and base added
flowed through the two instrument cells in series
with a delay loop in between. The instrument base-
line was periodically established using a distilled
water feed. Early instrument malfunction was traced
to improper electrical grounding of the ground wire
in the power line. This was corrected by separate
grounding of the instrument and recorder cases.
Unfortunately, the instrument became operational
only in time for the last pilot run. Although good
data were obtained over a significant portion of
this run, a number of instrument defects were
apparent which need correction before the instrument
can qualify for field use.

These defects and their correction will be discussed
later. The Abcor run started at about 1:00 P.M. on
Thursday, August 28, and was completed at about 8:00
A.M. the following morning. The bulk of the useful
Amicon data was obtained between about 10:30 P.M.
Thursday evening and 3:30 A.M. Friday morning. Xerox
copies of the recorder traces for these data are
presented in Figure 19. Tabulations of recorder
readings and "Δ OD" numbers derived from these
recorder traces are presented in Table I along with
TOC readings from the Ionics monitor and TOC data
obtained subsequently at Amicon using a Technicon/
Phase Separations Tocsin I Analyzer. Recorder
readings for the stream, W, refer to operation with

FIGURE 19

TOC = 7.4

-42-

0301 TOC = 7.4

0254 shuttle waste
P = 15 psi

Page 1
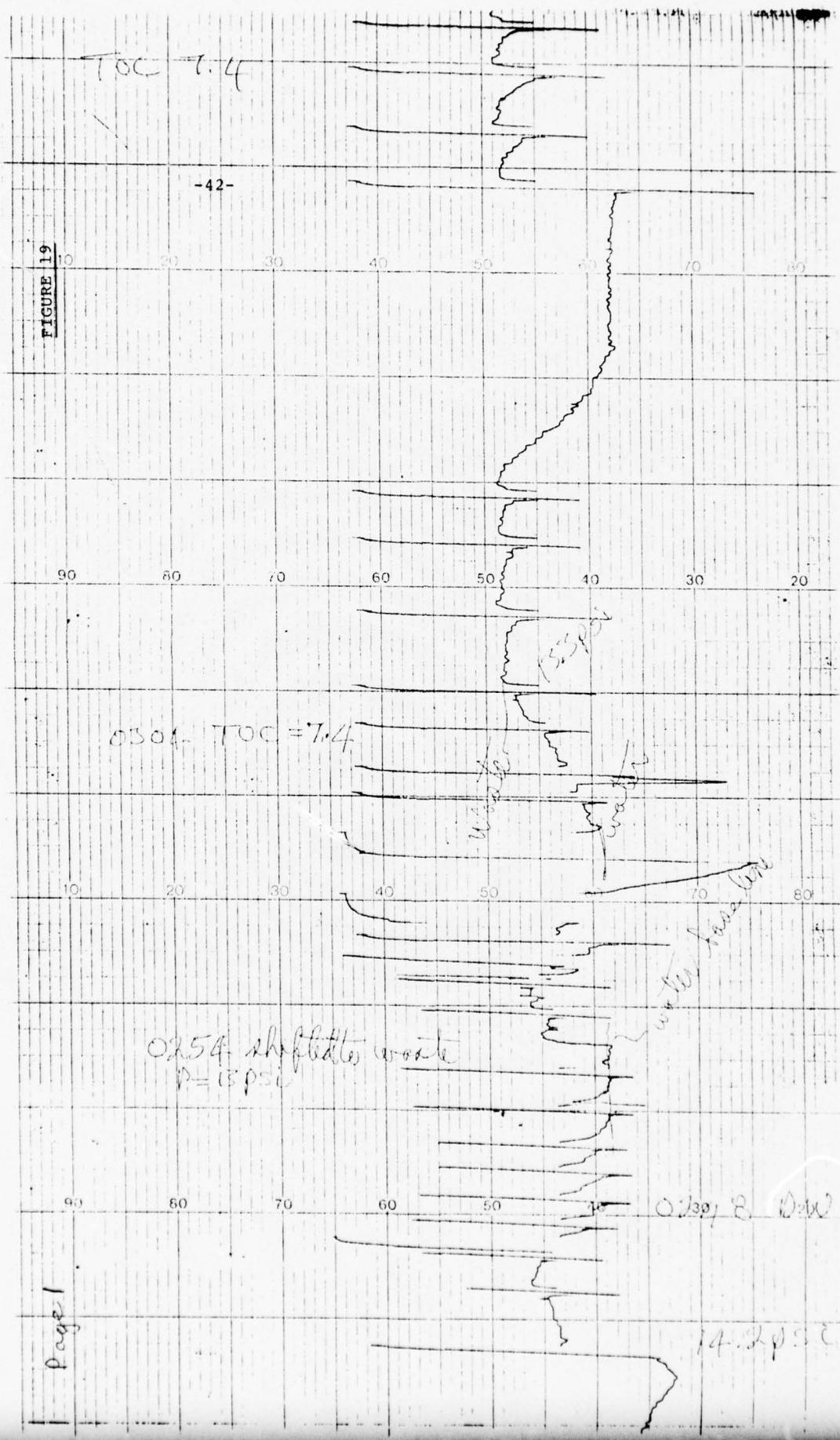
TOC = 8.3

-43-

TOC = 7.2

10   20   30

TOC = 7.0

Switch to waste
3356

90   80   70   60   50   40   30   20

TOC = 7.0

13.0 psc

TOC 7.0

10   20   30   40   50   60   70   80

0343   Drifted to D.W
P = 15.2
TOC 7.3

TOC 7.3

TOC 9.3

90   80   70   60   50   40   30   20

Purged   TOC 7.4

$OC = 8.9$

| 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 |

$OC = 8.4$

$OC = 8.8$

$OC = 8.5$

| 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 |

$OC = 8.6$

$OC = 8.3$

| 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 |

$OC = 8.4 - 0502$

$OC = 8.0 - 0457$

$OC = 8.1$

| 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 |

0450

$OC = 8.0$

| 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 |

0507

This rise is due to increased KMnO$_4$ concentration in inlet cell due to inlet pressure decrease – outlet still diluted KMnO$_4$

Rise due to reacted waste appearing in outlet cell

Baseline ref. again, same concentration of more concentrated KMnO$_4$ in distilled water in both cells.

This rise is due to diluted, reacted waste appearing in outlet cell. The reading is lower than the reading before the switch to distilled water for two reasons:
(1) the reactants are diluted by the pressure ratio, 13.0/14.3;
(2) the waste is diluted by distilled water, due to interface mixing during flow through the inlet tubing.

This drop is due to distilled water appearing in the outlet (same KMnO$_4$ concentration in both cells)

This drop is due to decrease in KMnO$_4$ concentration in inlet cell due to increase in water pressure.

-49-

$TOC = 8.2$ 0656

$TOC = 8.4$ 0651

$TOC = 8.4$ 0646

$TOC = 8.3$ 0641
0740

$TOC = 8.8$ 0636

$TOC = 8.6$ 0631

$TOC = 8.7$ 0626

Baseline shifted from runs on pages 8 and 9.

-51-

Baseline shifted for runs on Pages 8 and 9

TABLE I

RECORDER OUTPUT READINGS

Δ OD = 1.0 $\simeq$ 10 ppm acetaldehyde

Time	Stream	TOC	Monitor Reading	(Δ OD)	Time	TOC
1200						
0230	W	7.2	.48	.092		
0240	W	7.2	.475	.087		
0240	DW		.388			
0254	W					
0304	W	7.4	.488	0.100		
0325	W	7.4	.49	0.102		
					1530	6.1
0334	W	9.3	.51	0.113		
0343	W	7.3	.51	0.115		
0343	DW		.395			
0356	W					
0400	W	7.0	.50	0.105		
0405	W	7.2	.510	0.115		
0410	W	8.3	.525	0.130		
0415	W	7.7	.520	0.125		
0420	W	7.0	.51	0.112		
0425	W	7.6	.51	0.112		
0430	W	7.8	.51	0.112		
0435	W	7.9	.51	0.112		
0440	W	7.8	.51	0.112		
0445	W	8.0	.515	0.117		
0450	W	8.1	.510	0.108		
0455	W	8.0	.515	0.113		
0500	W	8.4	.520	0.118		
0505	W	8.3	.520	0.118		
0510	W	8.6	.520	0.118		
0515	W	8.5	.517	0.117		
0520	W	8.8	.521	0.121		
0525	W	8.4	0.318	0.118		
0530	W	8.9	0.320	0.120	1730	6.0,6.5
0535	W	8.8	0.520	0.120		
0540	W	8.6				
0545	W	9.0				
0550						
0555						
0600	DW		0.400			
0610	W	9.2	0.518	0.118		
0615	W	8.7	0.511	0.111		
0620	W	8.6	0.514	0.114		
0625	W	8.7	0.510	0.110		
0630	W	8.6	0.510	0.110		

TABLE I (continued)

Time	Stream	TOC	Monitor Reading	(Δ OD)	Time	TOC
0635	W	8.8	0.511	0.111		
0640	W	8.3	0.502	0.102		
0645	W	8.4	0.502	0.102		
0650	W	8.4	0.500	0.100		
0655	W	8.2	0.520	0.120		
0700	W					
0705	W	8.2	0.510	0.110		
0710	W					
0715	W	7.9	0.511	0.111		
0720	W	7.9				
0725	W	7.5	0.500	0.100		
					1930	5.8
	W	7.3	0.492	0.092		

MUST product water (to which permanganate and base
have been added) flowing through the two cells in
series. Recorder readings for the stream, DW, are
obtained with distilled water (to which permanganate
and base have been added) flowing through the two
cells in series. These latter readings represent
the instrument baseline--the output with no perman-
ganate oxidation occurring. The Δ OD column repre-
sents the difference between the readings with
the product water flowing through the distilled
water baseline. Since a 10 ppm acetaldehyde solu-
tion gives a Δ OD of about 1.0, the Δ OD of about
0.1 consistently obtained is equivalent to about
a one ppm concentration of acetaldehyde. In order
to obtain a uniform mixture entering the first cell
of the colorimeter, it was, however, necessary to
use a Kenics Static Mixer following the Vortex
Mixer. This introduced a time delay so that the
solution had about 30 seconds to react before
entering this first colorimeter cell. From Figure
11, the rate of acetaldehyde oxidation by permanganate
is such that with a solution of about one ppm
acetaldehyde, the oxidation would have gone about 25%
towards completion in 30 seconds. Thus, the readings
are really equivalent to an acetaldehyde concentra-
tion of about 1.5 ppm. Of course, if higher alde-
hydes are being oxidized only to the corresponding
acid, the permanganate readings correspond to a
higher ppm. One important conclusion from these
tests is that it does not appear necessary to use
a tracer with the permanganate colorimeter to
monitor the ozonation. Aldehydes appear to be pro-
duced and to accumulate naturally during ozonation.

From the rate of flow through the permanganate
monitor and the holdup in the tubing between the
tee into the TOC monitor supply and the second flow
cell in the colorimeter, a delay may be calculated
to determine what TOC monitor reading to compare
with the permanganate monitor reading. This delay
is equivalent to about 13 minutes; a permanganate
colorimeter reading should therefore be compared
with a TOC reading taken 13 minutes earlier. In
Table II data for the Ionics TOC monitor, the
permanganate colorimeter, and the Phase Separations
Tocsin I TOC Analyzer are compared for the three
samples in this time period for which Tocsin data
are available. Although there are data for the
permanganate monitor at close to the desired times
(10 minutes after the TOC readings) for comparative
evaluation, the data are not always available at
precisely corresponding times. From the trends of
the Ionics and permanganate monitor readings, how-
ever, the changes which are apt to occur in the

TABLE II

Run Time	Ionics TOC Reading	Technicon Phase Separations Tocsin I Reading	Permanganate Colorimeter Monitor Reading
1525	7.4		
1530		6.1	
1543			0.115
1725	8.4		
1730	8.9	6.2	
1735			0.120
1915	7.9		
1925	7.5		0.100
1930		5.8	

short time differences from direct correspondence
are small. From Table II it is apparent that there
is not enough variation in any of the data to es-
tablish whether a correspondence between TOC and the
permanganate colorimeter readings exists or not.
It is at least clear that such a correspondence is
not ruled out for MUST product water by these data.
The instrument does appear to have the required
sensitivity, particularly since the noise, once micro-
bubbles are eliminated, appears to be less than .01
OD which corresponds to about 0.1 ppm of acetaldehyde
and from Table II assuming the Phase Separations
Tocsin I measurements to be more accurate, to be
equivalent to about 0.6 ppm of TOC.

The response characteristics of the instrument may
be deduced from the recorder data by analyzing the
response when the feed is shifted from the MUST
product water to distilled water and then back again
to the MUST product water. A typical recorder trace
for this sequence together with an explanation for
the changes observed is shown in Figure 19. A
typical response is sketched below:
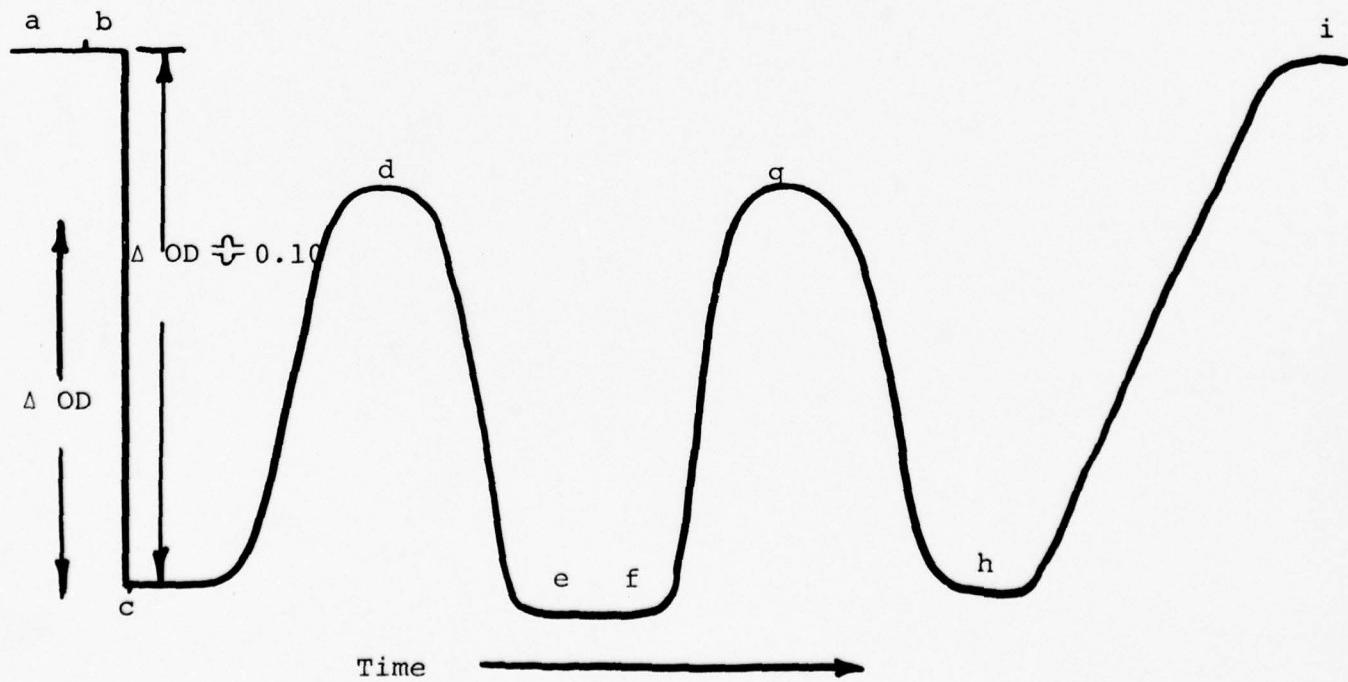
a = recorder reading with wastewater feed to colori-
meter. Gas pressure on KMnO$_4$ and KOH feed
streams $\approx$ 14.3 psig; pump pressure on waste-
water feed stream $\approx$ 13.0 psi. KMnO$_4$ feed stream
concentration and capillary diameters and
lengths are chosen to give a potassium perman-
ganate concentration of 72 mg/liter = 0.455
millimolar with the same pressure upstream of
all capillaries. With the pressure on the waste-
water being less than that on the permanganate
stream upstream of the capillaries, the
permanganate concentration before any oxidation/
reduction reaction will be

$$\frac{14.3}{13.0} \times .455 = 0.500 \text{ millimolar.}$$

b = feed shifted from wastewater at 13.0 psi to dis-
tilled water at 14.3 psi.

c = the diluted distilled water appears in the inlet
cell of the colorimeter. This generates a drop
in Δ (OD) of about 0.10. The calculated drop,
assuming no reaction in either the distilled
water or wastewater before flow through the
inlet cell:

$$\Delta \text{ (OD)} = \varepsilon \ \Delta\{MnO_4^-\}$$

where ε = extinction coefficient for permanganate
ion at 522 nm.

$$\Delta \text{ (OD)} = 2370 \ \Delta\{MnO_4^-\}$$

$$= 2370 \times .0455 \times 10^{-3}$$

$$= 0.108$$

The observed Δ (OD) of 0.100 is quite close to
this, but the agreement is good in part because
of two cancelling factors: (1) the wastewater
is partially oxidized and the permanganate
partially reduced when the wastewater permangan-
ate stream flows through the inlet colorimeter
cell; and (2) the distilled water contains some
organics which are apt to be oxidized prior to
flow through the inlet colorimeter cell.

d = diluted reacted waste appears in the outlet cell. Because of axial mixing, the rise is lower than would be expected with distilled water in the inlet cell and reacted waste in the outlet cell. The solution flowing through the outlet cell is a mixture of reacted waste and distilled water.

e = distilled water-permanganate solution appears in the outlet cell. This produces the distilled water baseline reference.

f = the feed is shifted from distilled water to wastewater.

g = This peak results from an increased concentration of permanganate ion in the inlet cell due to the decreased pressure on the wastewater stream. As the more concentrated wastewater stream enters the inlet cell, the rise in Δ OD is less than expected from the straight dilution effect due to reaction of permanganate with the wastewater prior to entering the inlet colorimeter cell.

h = concentrated distilled water in the outlet cell, concentrated wastewater in the inlet cell.

i = concentrated wastewater in the inlet and outlet cells.

Since the recorder paper speed is inches/minute, the time from shifting the feed to its appearance in full concentration in the outlet cell is seen to be about 13 minutes, while it first begins to affect the outlet cell reading in about 7 minutes. Back-mixing due to laminar flow pipeline mixing therefore gives a time spread of about 6 minutes from first appearance of the feed in the outlet cell to its passing through the outlet cell in full conentration. These times can be significantly reduced by shortening lines, but the delay line between the cells is of course required to ensure time for reaction. This delay line is coiled which generates a stable secondary flow which reduces axial dispersion[9]. Tighter coiling of a larger diameter tube can be utilized to increase the Dean number and thereby further minimize the axial dispersion in this delay line. Elevating the fluid temperature in this delay line will increase the reaction rate and decrease the required residence time in the delay line but will also increase the rate of decomposition of permanganate under the alkaline conditions in this delay loop.

1. Gas Evolution and Entrapment

A number of design modifications to the perman-
ganate colorimeter monitor appear desirable in
light of the operational experience obtained
with it thus far. The principal design change
called for is one to reduce gas evolution and
entrapment in the colorimeter cells, primarily
in the cell following the delay loop. The gas
probably resulted from a combination of:
permanganate oxidation; the slow decomposition
of permanganate under alkaline conditions[6];
dissolution of nitrogen used for pressurization
of the distilled water, permanganate and base
streams; and dissolved ozone and air evolution
from the ozonated MUST stream. The pressure
drop through the capillary flow restrictions
will clearly lead to some gas bubble formation
if the liquid is saturated with nitrogen at
the same temperature upstream of the capillaries.
The delay loop between colorimeter flow cells
appears to be a source of bubbles, probably both
due to nucleation and growth of bubbles from a
supersaturated solution, due to permanganate
oxidation and due to the slow breakdown of
permanganate under strongly alkaline conditions[6].
Buildup of manganese dioxide in the delay loop
or in other parts of the system will, of course,
aggravate the gas evolution problem because of
the autocatalytic nature of the decomposition
reaction. The flow cell configurations, with
leads into and out of the top of the cells, com-
pounds the problem because these cells are
effective bubble traps. A cell with flow inlet
at its base and flow outlet at its top should
do much to alleviate the entrapment of bubbles
in the cell.

2. Mode of Operation

Use of the single cell, two wavelength mode of
colorimeter operation discussed above would
appear to introduce substantial improvements:

a. the noise level in the output signal should
be significantly reduced since most of the
factors generating noise will affect both
wavelength cancelling out. Problems due to
microbubbles, manganese dioxide deposition
on the windows or scattering of the light
beam and fluctuations in flow rates should
be markedly diminished.

b. The operation is simpler and involves less
    equipment than the other possible modes of
    operation. There is no need for rapid
    mixing since the flow enters the colori-
    meter only after a suitable delay time for
    oxidation to occur.

c. Operation with 522 nm and 426 nm as the
    two wavelengths monitored produces a higher
    signal than with operation at one of these
    wavelengths and an isosbestic point or with
    wither of the single frequency modes of
    operation. Experimentally, about 4 moles
    of permanganate are found to react with
    each mole of acetaldehyde when permanganate
    is in excess and the concentration is
    sufficiently basic. Oxidation of acetaldehyde
    to acetic acid requires only two moles of
    permanganate per mole of acetaldehyde, so
    some carbon-carbon bond scission is occurring
    as well. The calculated changes in perman-
    ganate colorimeter OD with single cell opera-
    tion at 522 nm and 426 nm and reaction with
    1 ppm of acetaldehyde is compared in Table
    III with the Δ OD obtained monitoring either
    at 522 nm or at 426 nm with either a dual
    cell, single-wavelength mode of operation
    or a single cell, dual wavelength mode of
    operation where the second wavelength is at
    an isosbestic point.

The colorimeter was subsequently modified at
Amicon to convert it to the dual wavelength
mode of operation, with 522 nm and 460 nm (an
isosbestic point) chosen as the two wavelengths.
A flow-through cell with positive flushing was
introduced. These modifications essentially
eliminated the gas bubble entrapment problem
and reduced baseline noise to a small fraction
of 0.01 OD as may be seen from the recorder
tracing reproduced in Figure 20. The data
show that, even after the Kenics Mixer, small
concentration fluctuations due to incomplete
mixing are present. These are eliminated by
flow through the delay coil.

a. Instrument response

    Experiments were carried out to determine
    the instrument response as a function of
    the level of base concentration and the
    permanganate acetaldehyde ratio. Results
    are presented in Table IV. The calculated

TABLE III

CALCULATED Δ OD FOR 1 PPM ACETALDEHYDE

$$\Delta \begin{bmatrix} -D_{522} \\ +D_{426} \end{bmatrix}$$

ΔD_{522}

ΔD_{426}

0.298

0.180

0.118

FIGURE 20: TCS DUAL WAVELENGTH SPECTROGRAM OF {KMnO₄}
72 mg/l AT ROOM TEMPERATURE IN BASIC SOLUTION
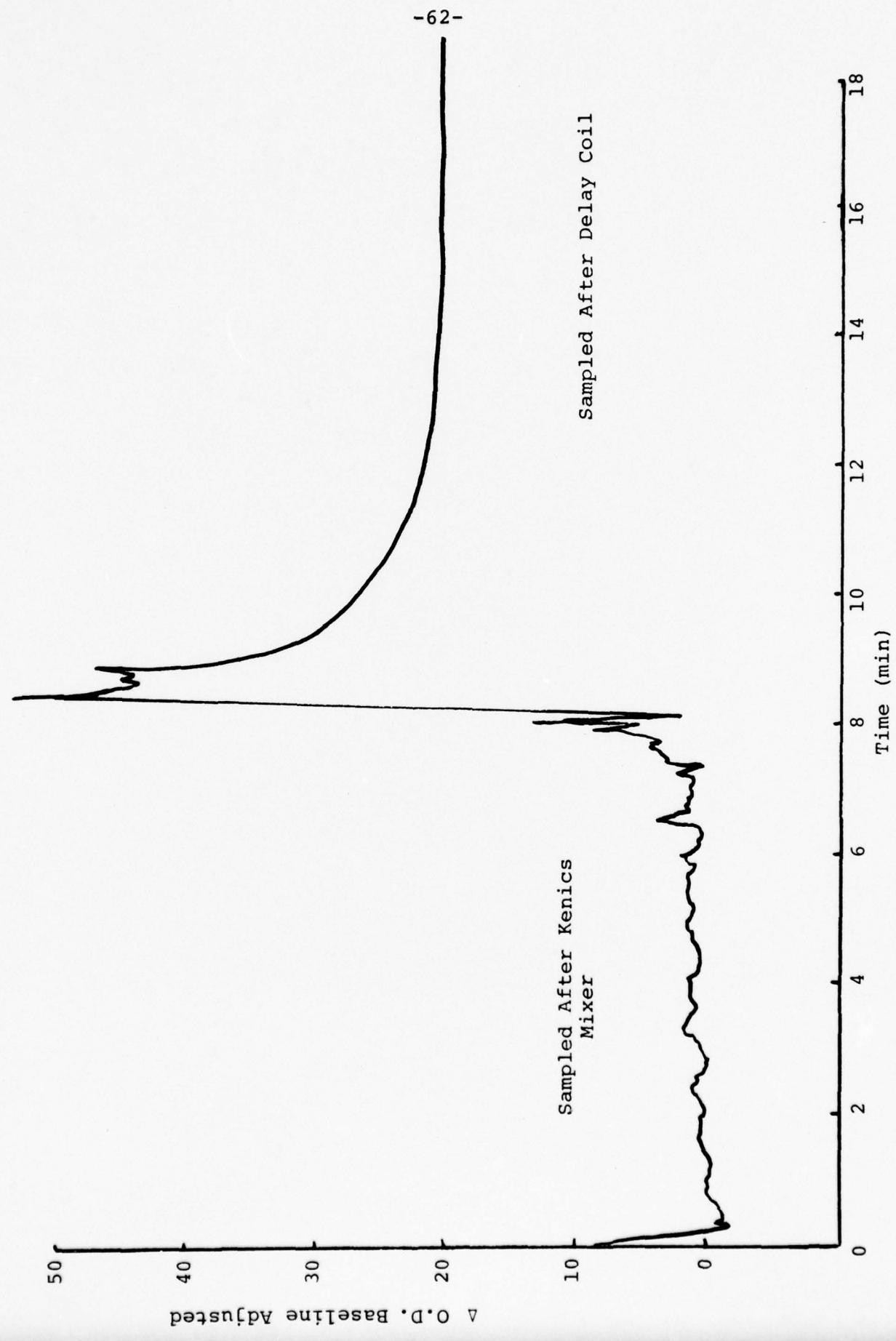
TABLE IV

Initial $\{MnO_4^-\}$ = 36 mg/l = 0.228×10^{-3} M

$\backsimeq$ 2.5 ppm CH_3COH if 4 mols MnO_4^- react with 1 mol CH_3COH

Calculated ΔOD			Experimental ΔOD			
ppm CH_3COH	$-D_{522}$ $+D_{426}$	ΔOD	$-D_{522}$ $+D_{426}$	0.1M $\{OH^-\}$	$-D_{522}$ $+D_{426}$	0.2M $\{OH^-\}$
0	-0.523		-0.522		-0.527	
0.42		0.126		0.127		0.131
1.00		0.298				
2.12		0.632		0.582		0.540
2.5		0.747				
4.24				0.812		0.775

and experimental agreement is good when only enough acetaldehyde is present to react with one-sixth of the permanganate, but is not as good when the acetaldehyde concentration is high enough to react with 80% of the permanganate. In Table V the range of optical densities are presented which would be observed with permanganate concentration sufficient to react with three different levels of acetaldehyde and a one cm path length cell. Optical densities above one become increasingly difficult to measure because of stray light, interference with the low levels of transmitted light. As the table indicates, if permanganate utilization is kept below 40%, and the correspondence between ozonated MUST TOC and permanganate is that observed in the limited experiments to date where one ppm of TOC reacts with about 0.2×10^{-4} moles of permanganate, then from 0 to 10 ppm of TOC can be monitored by noise, which in the dual wavelength mode of operation appears to be less than .002 OD by baseline drift which can be limited by frequent calibration and by permanganate decomposition which can be factored out. Conservatively, with baseline calibration every few hours, a sensitivity of .01 OD equivalent to 0.2 ppm of TOC should be readily attainable.

b. Instrument calibration

In the dual wavelength mode of operation, after flushing with bisulfite and rinsing with distilled water, the instrument baseline may be calibrated by introducing a neutral filter of known absorbance.

3. Flow Capillaries

The use of capillaries of selected diameters and lengths to control the flow ratios of the reactants appears sound, but the diameter of the capillary used to feed the permanganate should be enlarged. Its length should probably also be increased so as to maintain the same hydraulic resistance and it should either be folded back and forth or coiled to keep dimensions small. A larger diameter capillary will show less tendency to plug due to permanganate decomposition and will be easier to clean by flow or bisulfite through the system.

TABLE V

ABSORBANCE RANGE WITH A 1 CM PATH LENGTH AND 4 MOLS MnO_4^- PER MOL CH_3COH

Range of acetaldehyde
concentrations to be
monitored

Lower Limit		Upper Limit	D_{522}	D_{426}
ppm-CH_3COH				
0	-	2.5	.540 - .072	.018 - .296
0	-	5.0	1.080 - .144	.036 - .592
0		10.0	2.16 - .288	.072 - 1.184

$$\frac{ppm\ CH_3COH}{ppm\ TOC} \approx \frac{1}{5}$$

$$\frac{\Delta\ OD}{ppm\ TOC} \approx \frac{0.3}{6} = .05$$

If MnO_4^- utilization is kept to 40% to prevent MnO_2 formation, a high enough MnO_4^- concentration to react with 5 ppm CH_3COH will permit determination of 0.4 x 5 x 5 = 10 ppm TOC with a 1 cm path length and a sensitivity of about 0.2 ppm TOC.

Precise control of the permanganate concentration in the monitoring stream is a prerequisite for reliable monitoring. This requirement is considerably alleviated by operation in the dual wavelength mode with 426 nm and 522 nm, the two wavelengths monitored, since the absorbance at 426 nm results almost entirely from reaction with contaminant and is essentially proportional to contaminant level (for contaminants of a given reactivity level).

To control the permanganate/sample ratio more accurately, it may be desirable to pump the sample into a container which is pressurized by the same gas pressure used to drive the permanganate through its flow capillary. Limit switches would be used to control the liquid level in the container, and the container volume would be kept small to minimize the time lag it introduces.

4. Pressure Measurement

Replacement of the present Bourdon tube-type pressure gauges by electromechanical (piezo-electric or semiconductor) gauges will eliminate dead spot regions where permanganate can slowly decompose and release manganese dioxide into the system. Measurement of pressure after the metallic filters may prove unnecessary, particularly if a periodic bisulfite cleaning flush schedule is set up.

5. Instrument Simplification and Cost Reduction

Considerable simplification and ruggedization of the permanganate colorimeter is desirable and should be feasible once the desired characteristics have been pinned down.

D. Rate of Decay of Ozone

An alternate technique for monitoring the ozonation reactor is to monitor the rate of decay of ozone concentration in the effluent from the reactor. This can be done spectrophotometrically since ozone has a molar absorptivity of 2500 to 3000[10] at 360 mμ using a long (10 cm) path cell to obtain the desired sensitivity. The rate of decay of ozone concentration may be represented approximately by the equation:

(1)

$$\frac{-dO_3}{dt} = k_2 (O_3)(TOC) + k_d e^{-\frac{14.6}{RT}} (O_3)^{3/2}$$

The first term on the right represents the rate of oxidation of TOC and is a reasonable empirical approximation for typical waste streams, particularly for intermediate ozonation times[1, 11, 12]. The rate constant, k_2, is of course a function, both of the organic material present, the pH, and catalyst (e.g., UV) concentration. The second term on the right represents the rate of auto-decomposition of dissolved ozone as given by Li et al[13]. The rate constant, k_d, is also a function of pH, catalyst concentration, and ionic strength. For product water which has been treated with both reverse osmosis and ozonation, however, k_d should be essentially constant since the pH will be close to neutrality and since the impurity levels are quite low.

For very low impurity concentrations, the rate of decay of ozone concentration will be determined solely by the rate of autodecomposition; as impurity levels are increased, the rate of decay of ozone concentration will increase due to the first term on the right-hand side of equation (1), provided the impurities react with ozone. Measurement of the rate of decay of ozone concentration will then provide a measure of whether material which is oxidizable by ozone remains in the system.

To provide a preliminary indication of the utility of this concept, experiments were conducted with both distilled water and secondary effluent RO permeate, monitoring the rate of decay of ozone concentration in a long path (10 cm) cell at 254 nm and at room temperature ($\approx 25^\circ$C) as a function of ozonation time. Results are presented in Table VI and Figures 21, 22, and 23. As may be seen, the ozone rate of decomposition in distilled water shows the three-halves dependency on ozone concentration found by Li[13] and the zero time extrapolated intercept agrees with the solubility data of Rawson[14]. The relatively low OD readings at early times are probably attributable to Beer's Law deviations at high concentrations due to stray light interference in the Coleman 139 Spectrophotometer. The two different intercepts are probably partially attributable to a difference in temperature, but the data for the sample ozonated one hour (circular data points, Figure 1) are believed more accurate.

TABLE VI - PART A

DECOMPOSITION OF OZONE IN DISTILLED WATER

Absorbance monitored at 254 nm in a 10 cm path length cell

500 ml of water ozonated 30 minutes at room temperature with oxygen containing 38 mg/l ozone

TIME	OD	$(OD)^{-1/2}$
7	0.23	
10	0.25	2.0
20	0.22	2.13
40	0.21	2.18
55	0.18	2.35
120	0.076	3.63
130	0.070	3.78
145	0.060	4.08
175	0.040	5.00
205	0.035	5.35
265	0.025	6.33

TABLE VI - PART B

DECOMPOSITION OF OZONE IN DISTILLED WATER

500 ml of water ozonated one hour at room temperature (~25°C) with oxygen containing ~38 mg/l ozone

Absorbance monitored at 254 nm

TIME	OD	$(OD)^{-1/2}$
5	0.242	2.03
15	0.232	2.07
30	0.195	2.27
45	0.153	2.56
60	0.128	2.80
75	0.105	3.09
90	0.088	3.38
105	0.075	3.65
120	0.062	4.01
135	0.054	4.31
153	0.047	4.60
167	0.042	4.88
190	0.036	5.27

FIGURE 21

OZONE AUTODECOMPOSITION IN DISTILLED WATER AT ROOM TEMPERATURE ($\sim 25^{\circ}$C)

+ ozonated 30 minutes with gas containing 38 mg/l O_3 at room temperature

O Ozonated 1 hour with gas containing 38 mg/l O_3 at room temperature

$$(OD)^{-\frac{1}{2}} = 1.70 + .0189t$$
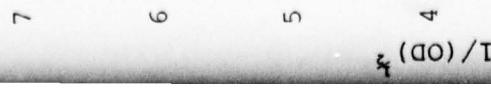
For molar absorptivity $\epsilon \simeq 2500$ l/g mole cm (1)

Ostwald coefficient $l = 0.17$(7), $l = 10$ cm

$(OD)_{t=0}$ in equilibrium with 38 mg/l of $O_3 = 0.336$

$\therefore$ cole $(OD)^{-1/2}_{t=0} = 1.72$

TIME (minutes)

$1/(OD)^{\frac{1}{2}}$

FIGURE 22

DECOMPOSITION OF OZONE IN SECONDARY EFFLUENT

Ozonated one hour at room temperature with oxygen containing 38 mg/1 ozone

$(OD)^{-\frac{1}{2}} = 1.20 + .0207t$

-70-
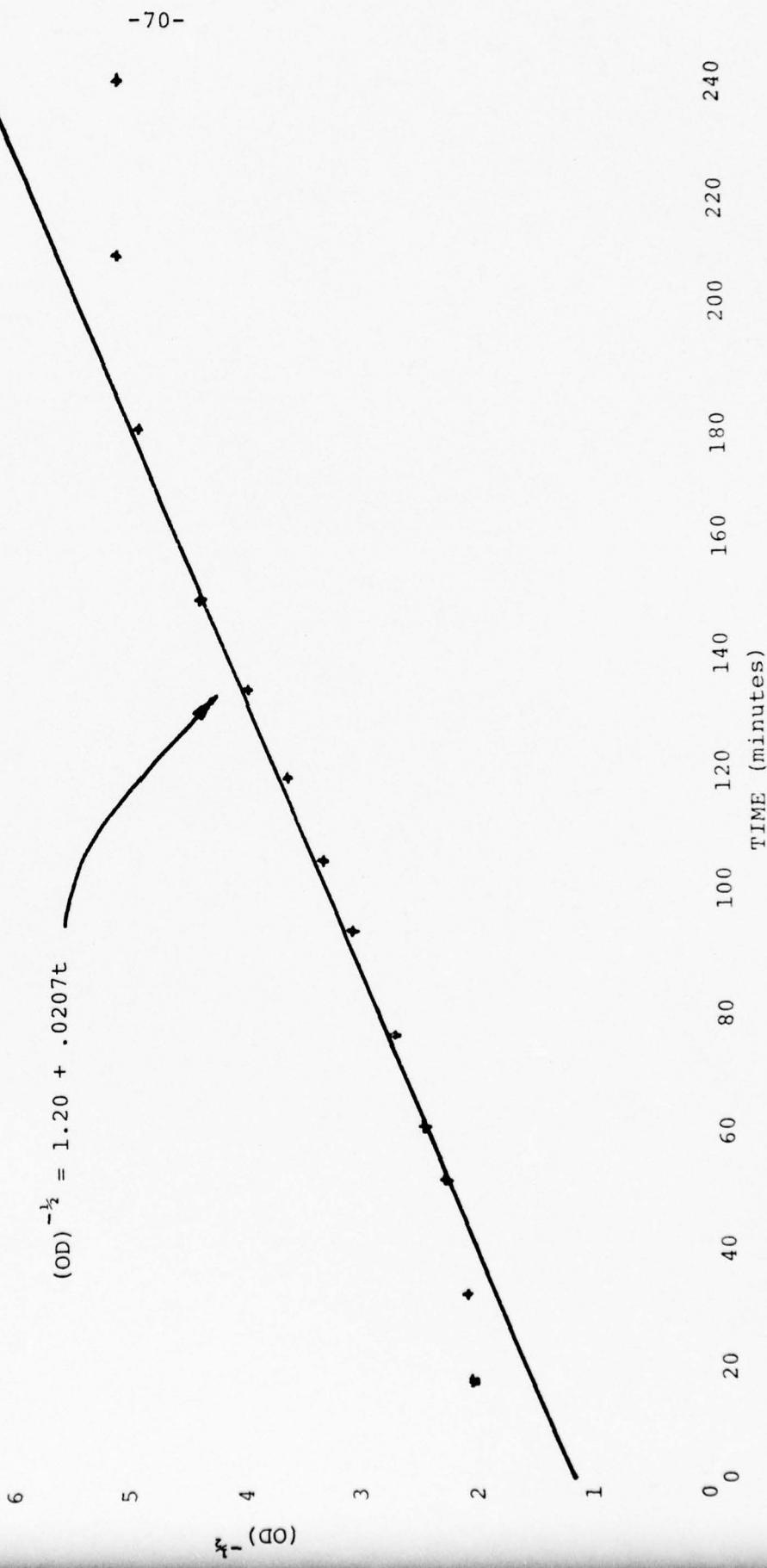
FIGURE 23

RATE OF DECAY OF OZONE IN DISTILLED WATER
AND SECONDARY EFFLUENT RO PERMEATE AT
ROOM TEMPERATURE

$$2.303 \log \frac{OD_1}{OD_2} = K \, \Delta t$$

	O_3 Treatment	$[O_3]$ mg/l	$K(\min^{-1})$
O Dist. H_2O	Saturated	38	.0118
□ 2ndy effl.	Saturated	38	.0312
△ Secondary Effluent	30 min. in reaction vessel	38	.0193
X Secondary Effluent	60 min. in reaction vessel	38	.0130
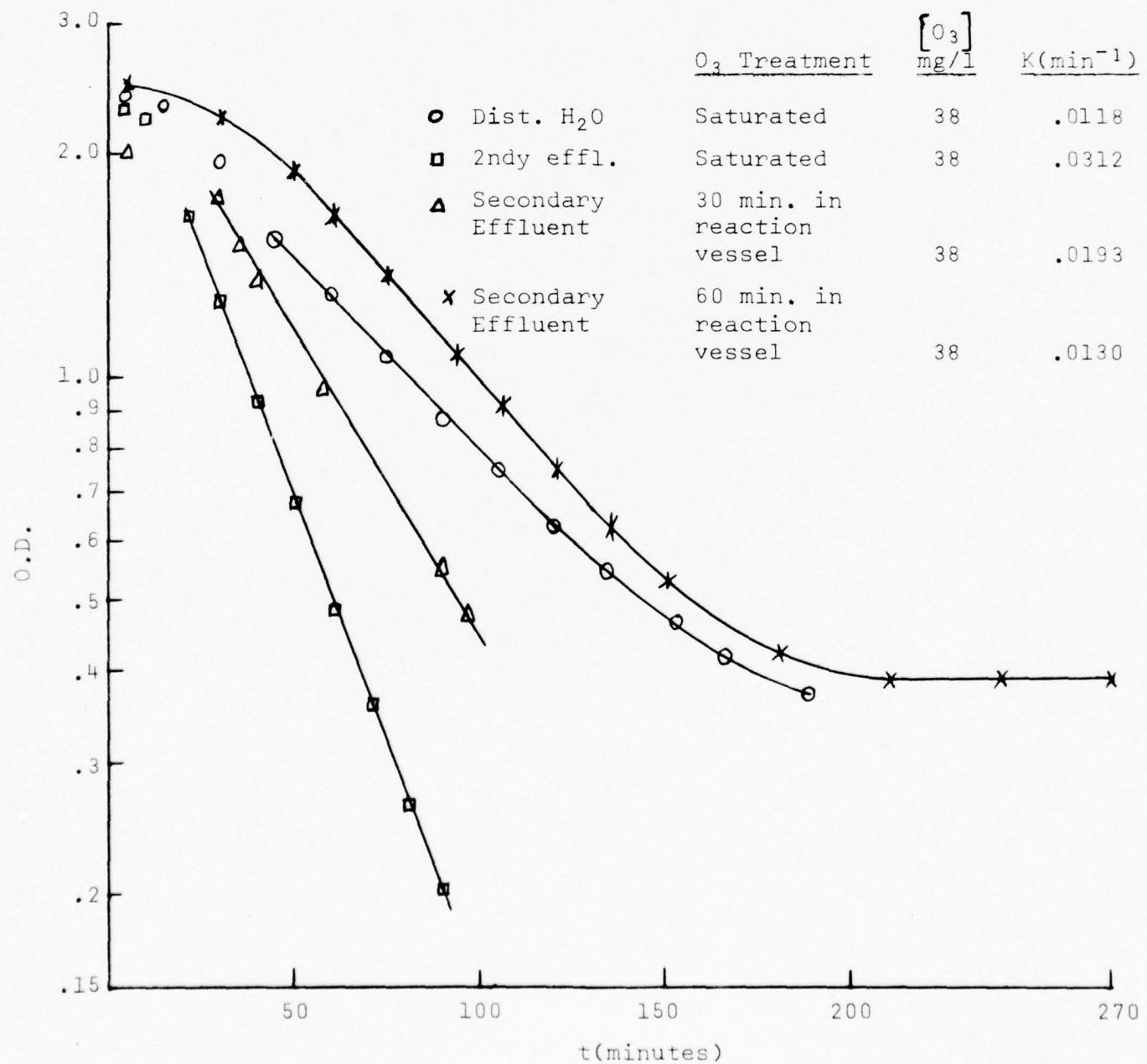
With the secondary effluent, the rate of decay of
ozone concentration is clearly higher than with
distilled water, particularly for material ozonated
for less than one hour. The effluent contacted
with ozone for a few minutes to saturate it and that
ozonated for 30 minutes both show rates of decay
dominated by the rate of oxidation of TOC (first
right-hand term in Equation 1). The zero time
intercepts for these data are again in approximate
agreement with the Rawson solubility data[14]. For
secondary effluent ozonated at room temperature
for one hour, the rate of decay of ozone (Figures
2 and 3) is only slightly greater than in distilled
water and the further purification achievable with
room temperature ozonation in a reasonable time
period is therefore small.

To evaluate the true potential of this monitoring
technique, low holdup flow cells should be utilized
and measurements at higher temperatures, where
reaction rates are faster, should be investigated.
The technique appears to hold promise.

IV.   CARBON ADSORPTION EXPERIMENTS

Three primary processing steps presently contemplated
for the purification of MUST water are RO treatment,
ozonation and adsorption by activated carbon. In
order to investigate the adsorption characteristics
of activated carbon relative to MUST RO permeate,
adsorption isotherms were studied for both ethanol
and acetaldehyde. Ethanol was selected as a known
principal impurity in the MUST RO permeate. Acetalde-
hyde was selected as a principal contaminant in ozonated
MUST RO permeate.

A.   Experimental Procedures

A 790 ppm solution of ethanol was prepared by
adding 1 ml of ethanol to 1,000 ml of distilled
water. This solution was added to a reaction
flask. One hundred grams of previously-washed
Pittsburgh Charcoal 20/50 mesh was then added to
the reaction flask. This solution was then agitated
overnight on a rotary mill. The following day the
charcoal was removed by using a Buchner Funnel with
suction and Whatman #1 Filter Paper. A sample of
the filtrate was then analyzed and the ethanol
concentration determined as usual by the acidified
dichromate method. This entire experiment was
carried out at room temperature. The same experi-
ment was repeated at $60^{\circ}C$. The solution was stirred
overnight in a reaction vessel at $60^{\circ}C$ and filtered
hot before being analyzed for ethanol concentration.
A third experiment was carried out at room
temperature with a 800 ppm solution of acetaldehyde.
The acetaldehyde concentration was determined by
reacting it with basic potassium permanganate as
described previously in this report. The results
are represented in Table VII.

Two more carbon adsorption experiments were performed
and both times a Pyrex glass column was used since
this setup is more in line with the actual processing
step than batch-type experiments. In the first
column experiment 114 g of activated carbon were
added to a 1" I.D. x 2' long Pyrex column with a
fritted glass base. The carbon filled approximately
10" of the column. The column was filled with
distilled water and then four liters of a 79 ppm
ethanol solution were passed through the column at
room temperature at a flow rate of 20 ml/minute.
Small samples of about 20 ml were collected every
250 ml, analyzed for ethanol using an acidified
potassium dichromate colorimeter test. A second

TABLE VII

DECOMPOSITION OF OZONE IN SECONDARY EFFLUENT RO PERMEATE

700 ml of secondary effluent (Brockton) RO permeate
was ozonated for one hour at room temperature with
oxygen containing 38 mg/l of ozone, and the
absorbance then monitored at 254 nm in a
10 cm path length cell

Time	OD	$1/(OD)^{1/2}$
0	~0.25	
15	0.235	2.06
30	0.225	2.11
50	0.192	2.28
60	0.165	2.47
75	0.137	2.71
93	0.107	3.06
105	0.091	3.31
120	0.075	3.65
135	0.063	3.98
150	0.053	4.35
180	0.042	4.88
210	0.039	5.06
240	0.039	5.06
285	0.039	5.06

identical experiment was performed with slightly less activated carbon, i.e., only 73 grams of activated carbon were used. The results are presented in Figure 24.

B. Discussion of Results

From the effluent curves, the total alcohol adsorption on the activated carbon may be estimated and a distribution coefficient for alcohol between the carbon and the solution calculated and compared with those derived from batch experiments. These data are presented in Table VIII.

The adsorption experiments indicate (Table IX and Figure 25 and 26) that the batch equilibrium data fit Freundlich adsorption isotherms. The slight effect of temperature on ethanol distribution indicates a low heat of adsorption which is consistent with the relatively weak adsorption of the alcohol.

Acetaldehyde is somewhat more strongly adsorbed than the ethyl alcohol, which is consistent with the higher hydrogen bonding potential of the alcohol and its consequent greater affinity for water. The data indicate both ethyl alcohol and acetaldehyde can be adsorbed from MUST RO permeate using activated carbon columns but the low distribution coefficients indicate that the carbon would have to be regenerated frequently. With a distribution coefficient of α, the weight of carbon is at a minimum W/α. Thus, to process 3500 gallons of water with an alcohol distribution coefficient of 30, approximately 18 ft.^{3} of carbon would be required. With a volume of 18 ft.^{3} of carbon to process 3500 gallons of water, the carbon would have to be regenerated on a daily basis.

From the standpoint of monitoring, neither alcohol nor acetaldehyde is strongly adsorbed and either might be a suitable tracer material depending on the location of the activated carbon and the impurities which were to be removed by it. For example, if it were located after the ozonation step and were intended to remove substantially all residual impurities, then acetaldehyde might again prove to be a suitable tracer compound, both because it is likely to be the principal residual impurity and because it is not strongly adsorbed.

FIGURE 24: COLUMN ADSORPTION EXPERIMENTS
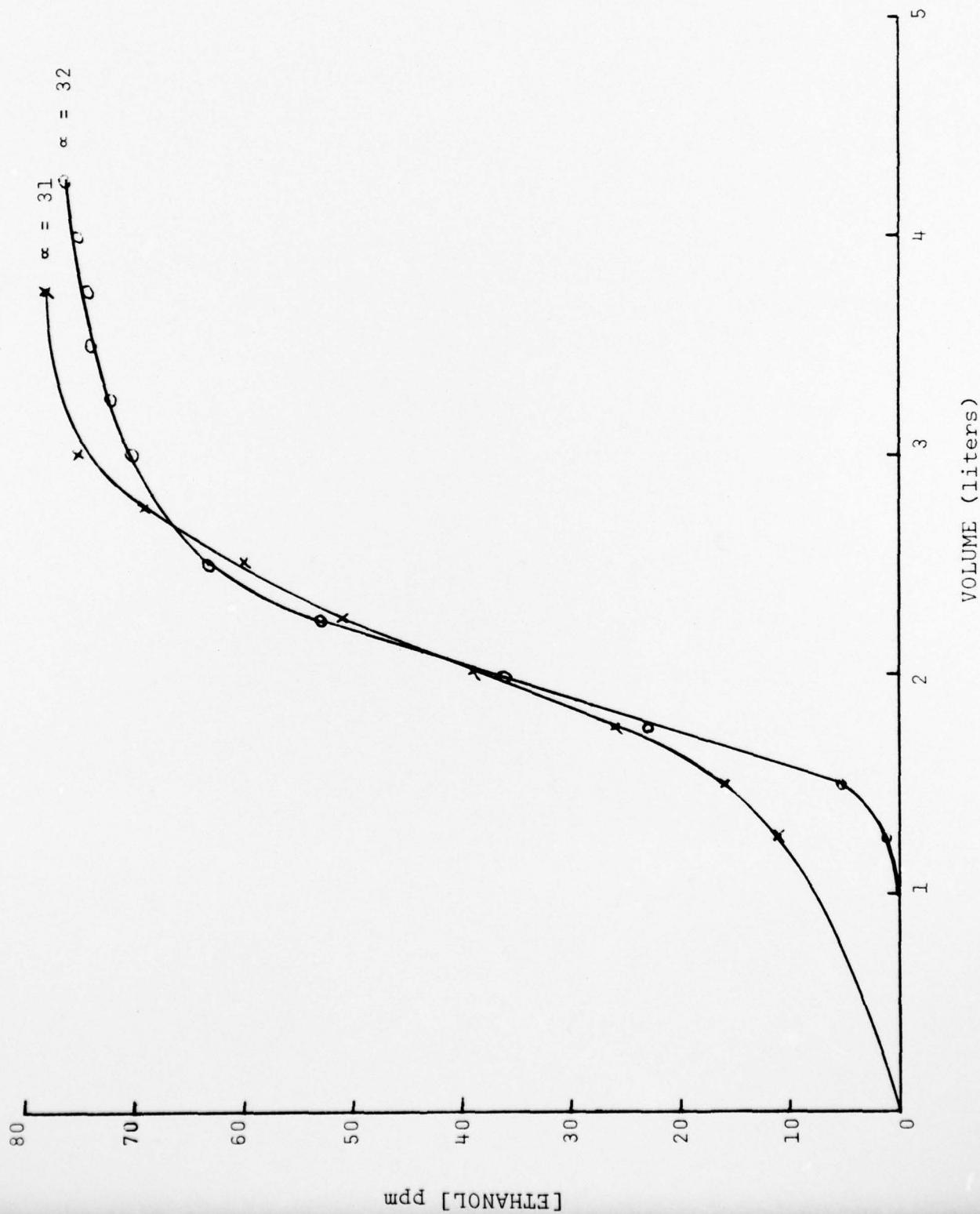
TABLE VIII

DECOMPOSITION OF OZONE IN SECONDARY EFFLUENT RO PERMEATE

One liter of permeate ozonated at room temperature
for 30 minutes with oxygen containing 38 mg/l ozone

Absorbance monitored at 254 nm in a 10 cm path
length cell using a Coleman 139 Spectrophotometer

Time (minutes)	OD	pH
5	>0.20	
20	0.175	
25	0.150	
30	0.135	
47	0.092	
80	0.055	
87	0.048	
~24 hours	0.0146	4.8

One liter of permeate contacted with gas containing
38 mg/l ozone for a few minutes to saturate it

Absorbance monitored as above

Time (minutes)	OD
5	0.020
20	0.0166
30	0.0126
40	0.092
50	0.068
60	0.048
70	0.036
80	0.026
90	0.020

TABLE IX

BATCH TYPE CARBON ADSORPTION EXPERIMENTS

Substance	Volume of H_2O (liters)	Amount of Carbon (gms)	Temp. (°C)	Before Adsorption [ppm]	After Adsorption [ppm]	
C_2H_5OH	1	100	25	740	240	$\alpha = 21$
C_2H_5OH	1	100	60	760	230	$\alpha = 23$
C_2H_5OH	1	100	25	50	13	$\alpha = 28$
C_2H_5OH	1	100	25	96	72	$\alpha = 30$
CH_3COH	1	100	25	800	170	$\beta = 37$
CH_3COH	1	100	25	51	8.5	$\beta = 50$
CH_3COH	1	100	25	100	18.5	$\beta = 44$

Equilibration Time ~17 hours

Column Adsorption Experiments

Substance	Temp. (°C)	Solution Concentration [ppm]	
C_2H_5OH	25	79	$\alpha = 32$
CH_3COH	25	~ 2	$\beta = 250$

Distribution Coefficient: $\alpha = \dfrac{\text{gms alcohol adsorbed/gms carbon}}{\text{gms alcohol in solution/gms water}}$

$\beta = \dfrac{\text{gms acetaldehyde absorbed/gms carbon}}{\text{gms acetaldehyde in solution/gms water}}$

FIGURE 25

FREUNDLICH ADSORPTION ISOTHERM FOR ETHANOL
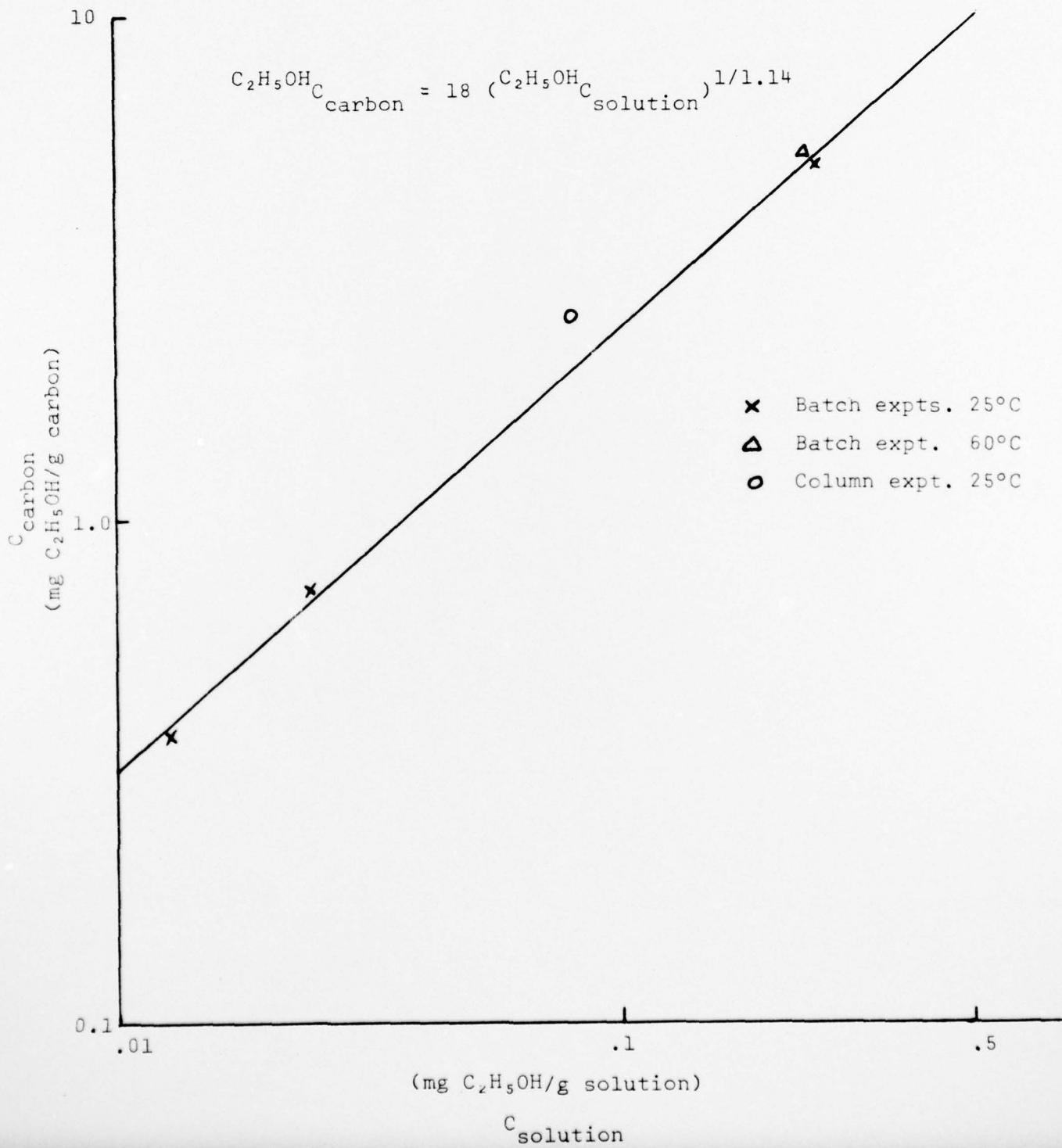
FIGURE 26: FREUNDLICH ADSORPTION ISOTHERM FOR ACETALDEHYDE

$C_2H_4O\ C_{carbon} = 30.5(^{C_2H_4O}\ C_{solution})^{1/1.10}$

Batch expts. 25°C
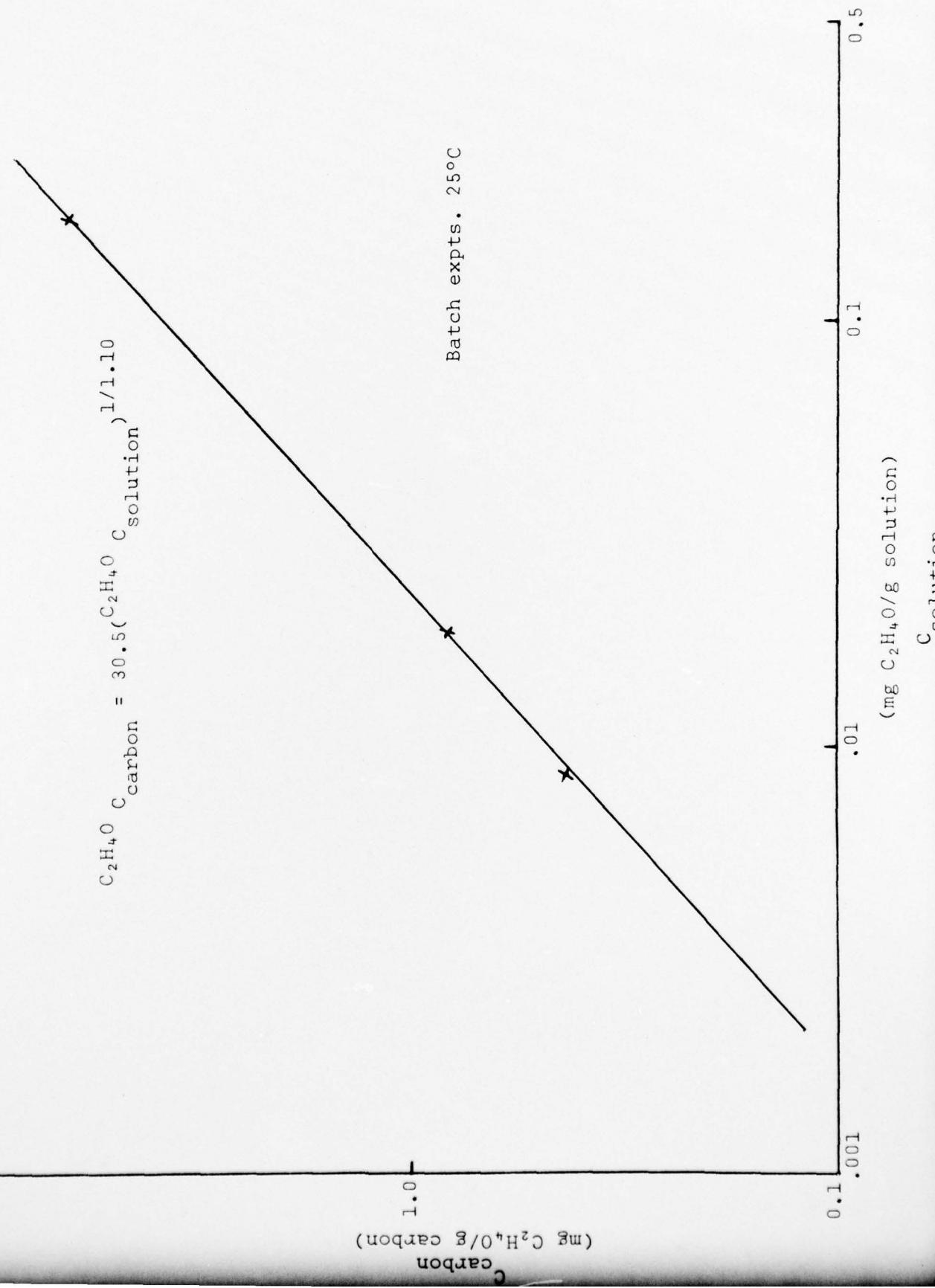
V.   SECONDARY EFFLUENT WASTE WATER STUDIES

Amicon has initiated studies for the monitoring of
reverse osmosis, ozonation, and activated carbon
treatment steps in various combinations for the
processing of secondary effluent of municipal waste
water to upgrade it to tertiary quality. Amicon
arranged to receive secondary effluent waste water
from the municipal waste treatment plant in Brockton,
Massachusetts.

A.   Pilot Plant - Construction and Operation

A pilot plant for the treatment of secondary
effluent waste water was constructed as shown in
Figure 27. The ten-gallon, stainless steel reser-
voir is filled with secondary effluent waste water.
With the appropriate valves open and shut, the
untreated effluent is transferred from the reser-
voir to the accumulator by pressurizing the reser-
voir with the aid of the nitrogen tank. Once the
accumulator is filled, the reservoir is isolated
from the system by closing the valves leading to
it. The whole system is then pressurized to
operating pressure via the nitrogen tank. The
tubing used to build the plant consists of 1/2"
stainless steel tubing except for the cooling coil
which is 5/8" stainless steel acting as a simple
heat exchanger. The pump used in this system is a
sealless magnet drive pump bought from the Kontro
Co., Inc. Since the recirculating pump has a
capacity of 20 gpm, which is considerably in excess
of that required by the RO unit, most of the waste
water is recirculated through the bypass loop, i.e.,
the cooling coil. The cooling coil is situated in
a large vessel which is filled with ice before each
run since an appreciable rise in temperature occurs
during the course of an experiment. The RO unit
was received from Universal Oil Products Company.
It is a spiral-wound, 620 mini-module with 1.0 sq.
ft. membrane area, producing 10.5 gfd with 96.6%
sodium chloride rejection at 600 psi, $25^{\circ}C$ and
5,000 ppm NaCl solution. The recommended flow rate
through the module is 2.0 gpm.

B.   Experimental Procedure

To five gallons of waste water enough sodium chloride
was added to make a 5,000 ppm solution. This solu-
tion was added to the reservoir and then transferred
to the accumulator and pressurized at 600 psi. Ice
was added to the cooling coil container and the pump
switched on. The flow through the RO unit was ad-
justed to 2 gpm and samples of approximately 20 ml

FIGURE 27

PILOT PLANT FOR SECONDARY EFFLUENT
REVERSE OSMOSIS TREATMENT
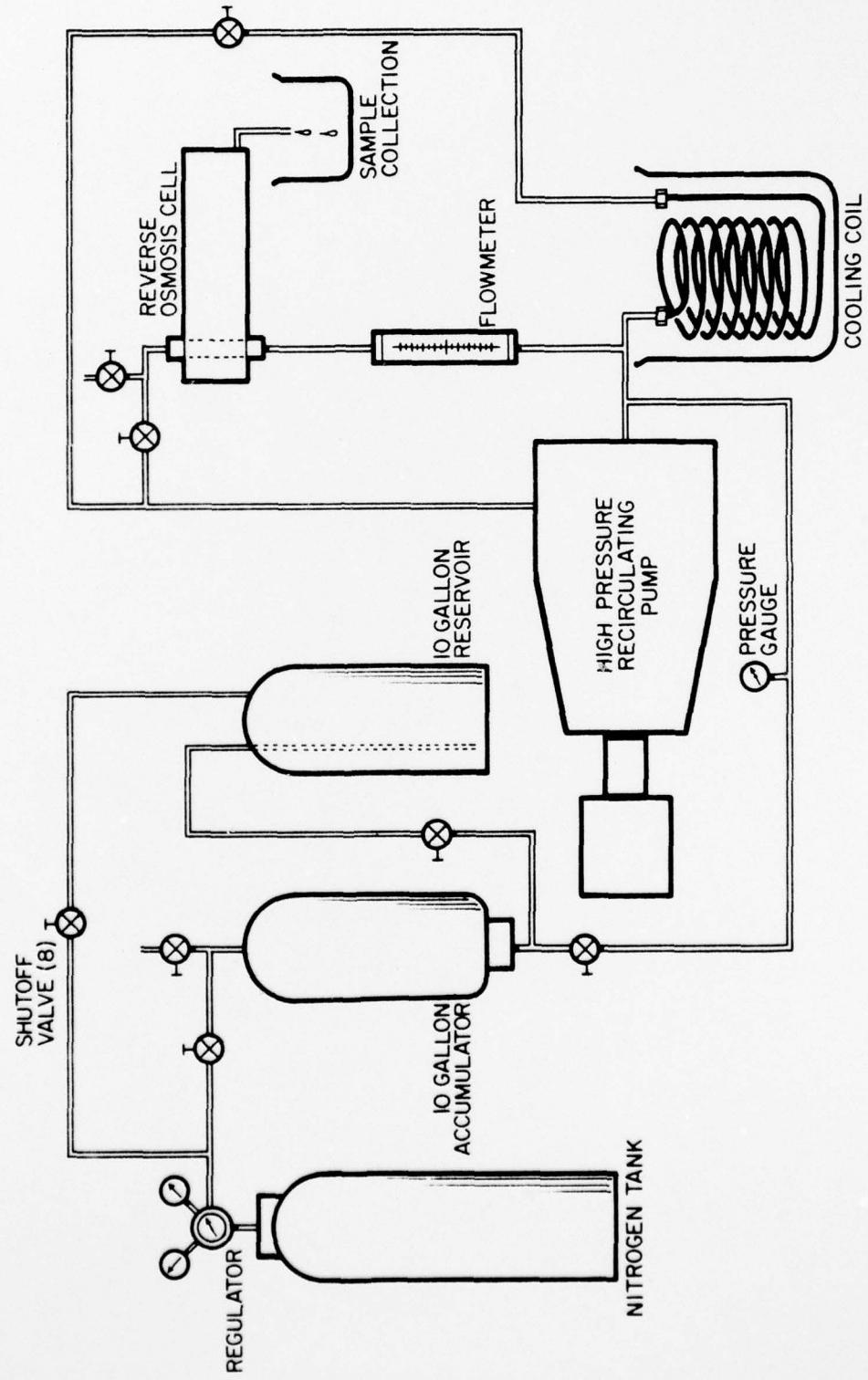
were collected for TOC analysis at two-liter intervals. A total volume of eight liters was collected. The results of this experiment are represented in Figure 28.

In a subsequent experiment, water from the Brockton waste treatment plant was again processed through the VOP RO module as before, and the RO permeate was then divided into three parts. The first was ozonated for 30 minutes at room temperature with oxygen containing 38 mg/l of ozone using the apparatus shown in Figure 1; the second was ozonated under the same conditions for 60 minutes; and the third was not subjected to further treatment. All three samples were then reacted with alkaline permanganate to determine whether a detectable change in OD would occur and all three samples were analyzed for TOC. Results are presented in Table X.

FIGURE 28: RO TREATMENT OF SECONDARY EFFLUENT WASTE WATER

Feed Concentration ≈ 33 ppm

RO module:	UOP 620 Mini-Module	UOP Data
Membrane area:	1.0 sq. ft.	
Temperature:	~25°C	
Pressure:	600 psi	
Flow rate:	2.0 gpm	
Flux:	10.4 gfd	10.5 gfd
NaCl rejection:	95.4%	96.6%

Permeate Concentration ≈ 7 ppm

[TOC] ppm

VOLUME (liters)

TABLE X

OZONATION OF RO PERMEATE OF SECONDARY EFFLUENT
FROM THE BROCKTON, MASSACHUSETTS, MUNICIPAL
WASTEWATER TREATMENT FACILITY

Sample	Ozonation Time (minutes)	Ozonation Temperature (^{o}C)	TOC
RO permeate	0	--	6.5
RO permeate	30	25	2.7
RO permeate	60	25	2.5
RO permeate	30	40	1.6
RO permeate	60	40	1.5

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